

Additional Practical Work



Additional Practical Work

CONTENT

Experiments

- I:** Synthesis of Aspirin
- II:** Chemical Investigation of Aspirin
- III:** Preparation of 2-chloro-2-methylpropane.
- IV:** Friedel-Crafts Alkylation: Synthesis of *p-t*-butyltoluene.
- V:** Friedel-Crafts Acylation: Synthesis of acetyl ferrocene.
- VI:** Preparation of Polystyrene.
- VII:** The Extraction of Trimyristin from Nutmeg.
- VIII:** A Multistep Synthesis: Preparation of 3-nitrobenzenecarboxylic acid.
- IX:** Preparation of an Azo Dye
- X:** Reduction using Sodium borohydride.
(Benzil to Hydrobenzoin)
- XI:** Kinetics: Hydrolysis of 2-chloro-2-methylpropane (t-butyl chloride)
- XII:** Potentiometric Redox Titration: Estimation of Iron(II) by titration against standard Dichromate solution.
- XIII:** Kinetics: Peroxodisulphate - Iodide reaction.
- XIV:** Preparation of Chrome Alum.
- XV:** Mini Project (Organic Based)
- XVI:** Preparation & Analysis of a Group IV Oxide (Lead(IV) Oxide)

continued:

Additional Practical Work

CONTENT **(continued)**

Experiments

XVII: Kinetics: Investigating the reaction between Permanganate and Oxalate.

XVIII: Preparation and Analysis of a Transition Metal Complex
Potassium trioxalatochromium(III) trihydrate.

XIX: Back titration: Estimation of Nickel by titration against EDTA

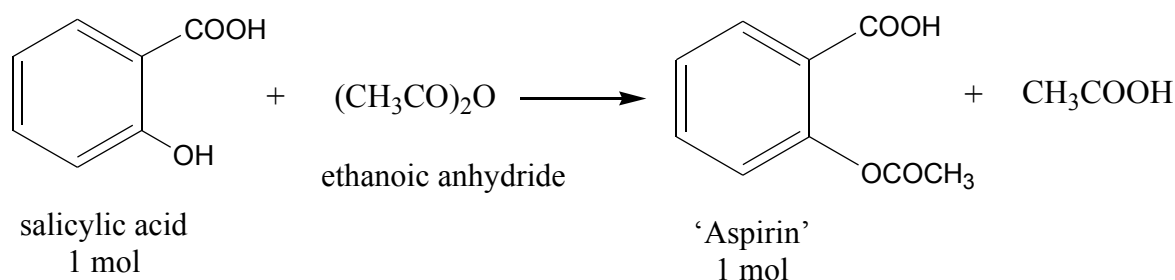
XX: To find the Molarities of Strong & Weak acids and their Enthalpies of Neutralisation by
Thermometric Titrations

Experiment I

Synthesis of 2-ethanoyloxybenzenecarboxylic acid (2-acetoxybenzoic acid, Aspirin).

The medicinal values of aspirin have been known for over 2000 years, however, prior to about 1860 the substance was administered in the form of herbal remedies (extracts of the leaves and bark of willow and poplar). Aspirin was first synthesised in 1853 by the French chemist, Charles Frederick von Gerhardt and manufactured by the Bayer Company in about 1900. Today some four billion tablets per annum are produced in the United Kingdom for the treatment of pain and fever resulting from a variety of medical conditions.

In this experiment aspirin is synthesised from 2-hydroxybenzenecarboxylic acid (salicylic acid):



Procedure:

1. 3g (0.022 mol) salicylic acid,
5g, (4.7 cm³, 0.05 mol) ethanoic anhydride
(**CARE: corrosive vapour, lachrymator**),
8 drops of phosphoric acid (85%)
an antibump granule

50 cm³ conical flask
- swirl contents & fit the flask with a condenser

2. heat the flask and its contents to 60°C on a water bath for approximately a quarter of an hour

water out

water in

support flask & condenser with clamps & retort stand
3. After heating add 4 cm³ of distilled water a little at a time, down the condenser, with swirling. **Care: The mixture may boil.** Allow the flask & mixture to cool to near room temperature.
4. **In a fume cupboard (with the fan on!)**

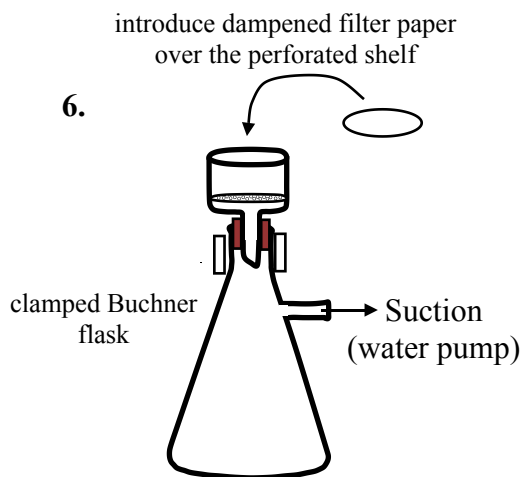
disconnect flask & pour contents into the water

50 cm³ distilled water

100 cm³ beaker
5. Stir the contents of the beaker whilst cooling with a trough of cold water.

solid aspirin forms in the mixture

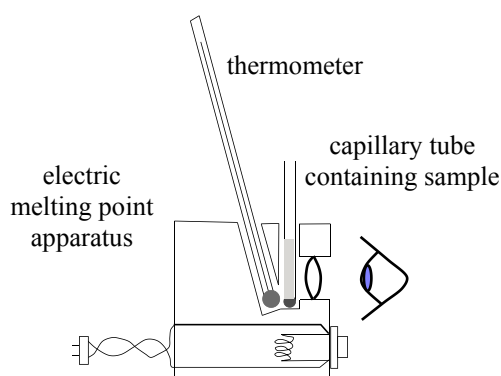
continued:



7. Pour the contents of the beaker into the filter funnel and isolate the crude aspirin.

8. Recrystallise the crude aspirin using about 10 cm³ of industrial methylated spirit (IMS). Dissolve the aspirin in the hot IMS (by *indirect* heating on a water bath; do **not** use a naked flame to provide heat). Pour this solution into about 20 cm³ of warm distilled water. If solid separates warm the mixture to give a clear solution and then allow the solution to cool slowly down to about 5°C. Filter off the purified aspirin. Dry in an oven at about 80°C and then weigh.

9. Measure the melting point of your dry, recrystallised, aspirin.



10. Calculate the % yield

$$\frac{\text{Mass obtained}}{\text{Mass of maximum theoretical yield}} \times 100$$

Suggest reasons for your % yield being less than 100%



Experiment 1

Synthesis of Aspirin

Example of Outcomes

Aspirin melts at 135°C. Melting point of recrystallised material = 134°C.

(**Note:** aspirin has a tendency to decompose at its melting point so you may find your recrystallised product melts over a range of about 4 degrees)

From the balanced equation, 1 mol salicylic acid (138g) gives 1 mol of aspirin (180g).

In a typical synthesis 2.50g of recrystallised aspirin was obtained.

% yield = $(2.50/3.91) \times 100 = 64\%$

The ir (KBr disc) shows intense absorption at 1750 cm⁻¹ & 1680 cm⁻¹ due to the ester/acid carboxyl groups (absorption position influenced by close proximity of the aromatic ring). Also, fairly broad absorption at approximately 3200 cm⁻¹ due to the OH portion of the carboxyl group.

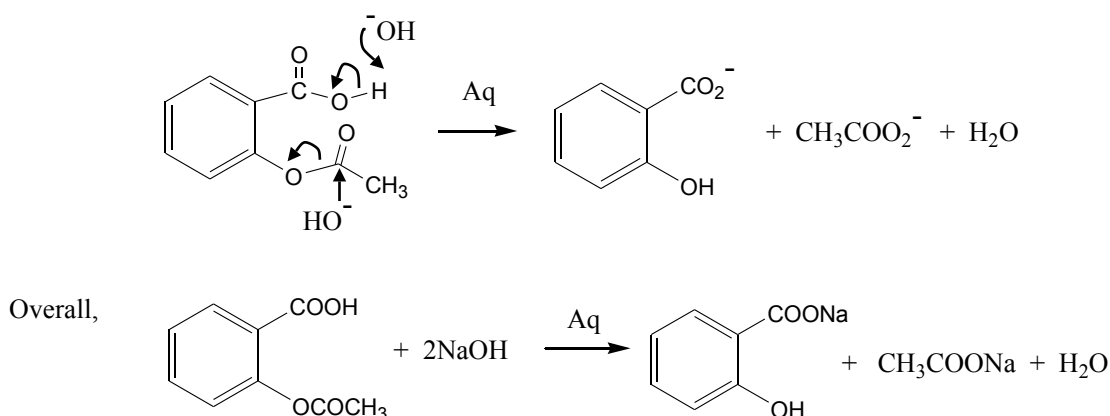
The pmr (10% in CDCl₃) shows a singlet above 10 ppm (approximately 11.5) due to the carboxyl proton, an aromatic multiplet at 7.5 ppm and a methyl singlet at 2.30 ppm.

Experiment II

Chemical Estimation of Aspirin

Back Titrimetric Method.

The % purity of your aspirin, from the previous experiment, can be estimated by reaction with sodium hydroxide solution. A quantity of aspirin is reacted with a known excess of standard sodium hydroxide solution. The excess alkali is then determined by titration against standard hydrochloric acid. Knowing that two moles of the base are required to react completely with one mole of aspirin it is possible to calculate the % aspirin in your product.



This estimation should be performed in duplicate and the mean result calculated.

very lightly grease the joint

water

250 cm³ flask

1. Weigh flask A accurately (m_1).
Add about 1g of the synthesised aspirin to the flask and weigh again (m_2).
2. To each of the flasks, A & B:
Add 20 cm³ of distilled water and 25.00 cm³ of standard 1M NaOH (**CARE: Caustic**).
Add a couple of anti-bump granules.
Attach the water condensers and heat on a hot water bath for 15 minutes with swirling.

very lightly grease the joint

'blank'

250 cm³ flask

3. Cool the flasks by running cold water over the outside. Pour 10 cm³ of distilled water down the inside of each condenser to ensure all the alkali transfers to the flasks. Disconnect each flask and titrate the contents against standard 1M HCl using 3 or 4 drops of **phenol red indicator (pH range: 6.8-8.4 changes colour from yellow to red)**.

The difference between the titre of the blank and the titre of the aspirin (V cm³) is the amount of alkali required in the reaction (the alkaline hydrolysis, *saponification*). With this result and making use of the equation for the reaction it is possible to calculate the percentage aspirin in the product.

Experiment II

Estimation of Aspirin

Example of Outcomes

Mass of 'aspirin' used: $m_2 - m_1 = w$ g

Difference between B & A titrations = V cm³ 1M HCl

Moles of hydrochloric acid used = $1.00 \times (V/1000) = V \times 10^{-3}$ = moles of sodium hydroxide reacted with the aspirin

Moles of aspirin hydrolysed = $0.5 \times V \times 10^{-3}$

Mass of aspirin hydrolysed = $180 \times 0.5 \times V \times 10^{-3}$ g

% purity = $[(180 \times 0.5 \times V \times 10^{-3}) / w] \times 100$

First attempt:

Synthesised aspirin sample, $W = 1.094$ g

Titre values: blank (B) = 24.10 cm³, sample (A) = 12.10 cm³

Difference, $V = 12.00$ cm³

% purity = $[(180 \times 0.5 \times 12.00 \times 10^{-3}) / 1.094] \times 100 = 98.7 \%$

Second attempt:

Synthesised aspirin sample, $w = 1.100$ g

Titre values: blank (B) = 24.15 cm³, sample (A) = 11.95 cm³

Difference = 12.20 cm³

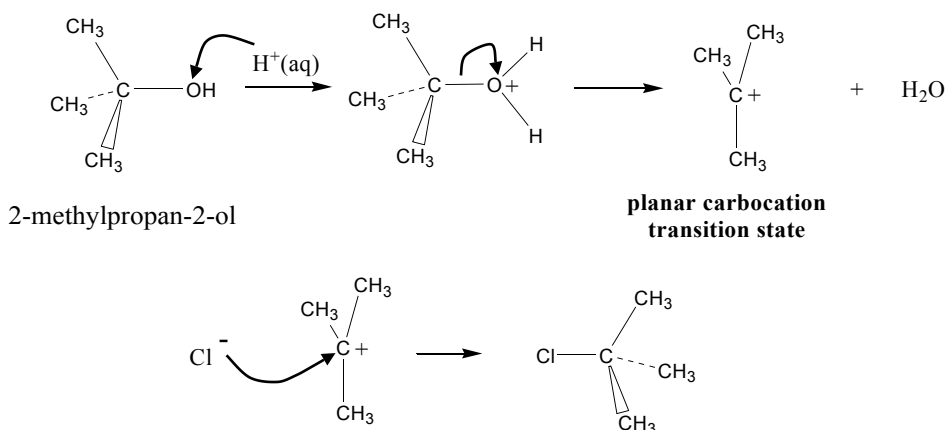
% purity = $[(180 \times 0.5 \times 12.20 \times 10^{-3}) / 1.100] \times 100 = 99.8\%$

Mean % purity = $(98.7 + 99.8) / 2 = 99.3\%$

Experiment III

The Preparation of 2-chloro-2-methylpropane (t-butyl chloride)

2-chloro-2-methylpropane is conveniently prepared by shaking 2-methylpropan-2-ol (t-butyl alcohol) with concentrated hydrochloric acid.



Procedure:

(NB: Due to the volatility of the product (t-butyl chloride) and one of the reactants (concentrated HCl) it is best to perform the following operations in a fume cupboard so as to avoid contact with the vapours)

1. 250 or 500 cm³ separating funnel-closed initially!

Add the following to the separating funnel:
About 5 g of anhydrous, *granular*, CaCl₂
Approximately 70 cm³ concentrated HCl
(CAUTION: corrosive fumes - support the funnel in a fume cupboard)
20 cm³ (0.21 mol) of 2-methylpropan-2-ol.

2. Gently swirl the funnel to mix the contents (**do NOT fit a stopper and shake at this stage**). The mixture may get warm as the reaction takes place & the gases inside the funnel will expand!

Once the initial reaction has taken place you can then fit a stopper

make sure the stopper fits the funnel snugly



and invert the funnel a few times periodically releasing the pressure inside the funnel by turning the tap in the usual way (check with your teacher if in doubt).

3. Run off & discard the aqueous layer

Add 20 cm³ of saturated NaHCO₃ solution & swirl the contents to gently mix. When evolution of CO₂ has ceased replace the stopper and carefully shake the contents (release pressure as necessary)

Run off aq layer and discard. If necessary, wash organic layer with more aq NaHCO₃. Discard washings. Then wash organic layer with about 15 cm³ of distilled water. Run off & discard the aq layer

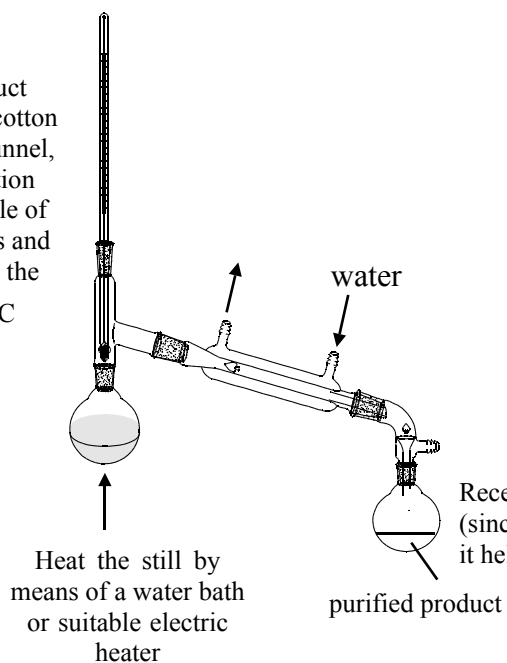
Run organic layer into a small conical flask and dry by adding a couple of spatulas of anhydrous sodium sulphate. Seal the flask with a **cork** and leave to stand for 5 - 10 mins. Swirl from time to time.

organic product
anhydrous Na₂SO₄

continued:

4. Distillation

Filter the product through a plug of cotton wool, in a small funnel, into the distillation flask. Add a couple of antibump granules and distil. Collect in the range 50 - 52°C



5. Weigh your purified product and calculate the % yield.
Store in a suitable, labelled, container.
Obtain an ir spectrum.

Receiver
(since the boiling point of the product is low
it helps to cool the receiver in a trough of iced water)

Experiment III

Preparation of 2-chloro-2-methylpropane

Example of Outcomes

Maximum yield = 0.21 mol (from 0.21 mol of t-butyl alcohol).

ie, $0.21 \times 92.5 = 19.4 \text{ g}$ (or 23.0 cm^3)

Actual yield = 14.5 cm^3 (or 12.2 g)

% yield = $(12.2/19.4) \times 100 = 63\%$

Apart from the possibility of incomplete reaction, one expects loss of product during the washing, isolation and purification procedures.

Mean boiling point of product = 52°C (lit. Value 51°C)

The ir spectrum shows peaks at: 2980-2850, 1450, 1385, 1155, 900 cm^{-1}

We expect C-Cl stretch at about 900 cm^{-1} . Most of the other absorptions are due to C-H stretching and bending in the methyl groups.

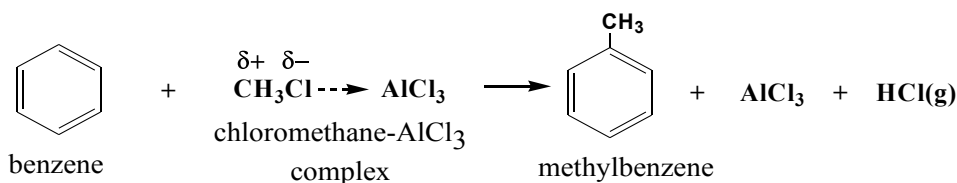
Experiment IV

Friedel-Crafts Alkylation

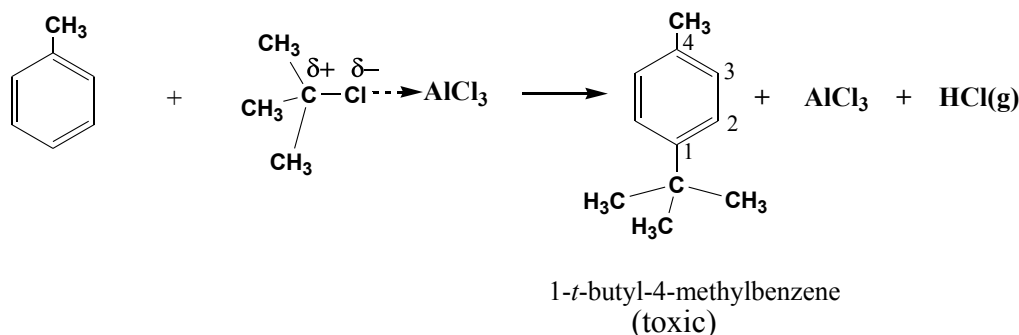
The Preparation of 4-(2'-methylpropyl)-1-methylbenzene (1-*t*-butyl-4-methylbenzene or *p*-*t*-butyltoluene)

The most generally useful method for introducing alkyl groups into an aromatic nucleus, such as that of benzene, is the Friedel-Crafts reaction. James Crafts was an American chemist and Charles Friedel a French chemist. The reaction was discovered when they were working together studying the effect of aluminium powder on certain chlorine containing carbon compounds. The reaction was investigated and developed between 1874 & 1891.

The simplest example of the reaction involves the reaction of chloromethane with benzene in the presence of anhydrous aluminium chloride. The aluminium chloride acts as a Lewis acid promoting the polarisation of chloromethane so that it reacts more readily with benzene.

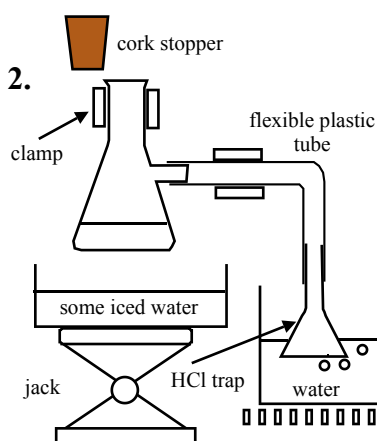
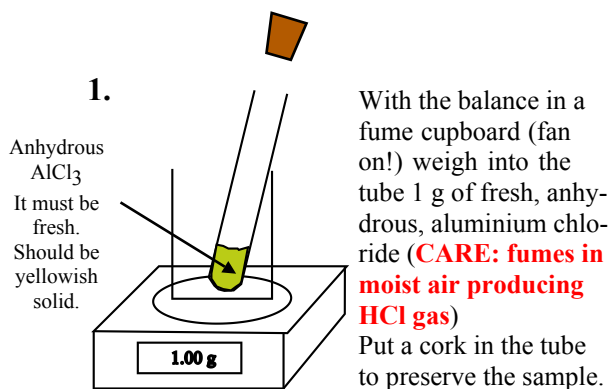


Since benzene is toxic (associated with the development of leukaemia) and chloromethane is a gas (bpt, -24°C at 1 atm) alternative reactants are used in the experiment described below. Methylbenzene (toluene) is used instead of benzene and 2-chloro-2-methylpropane (*t*-butyl chloride) is used in place of chloromethane.



Procedure:

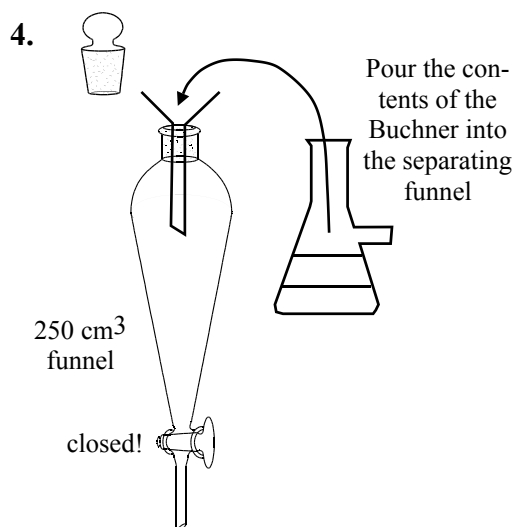
(NB: To avoid contact with inorganic & organic vapours, which can cause eye irritation and breathing difficulties, all stages of the preparation must be performed in a fume cupboard. Also wear safety spectacles and gloves)



Set up a small 100 cm³ Buchner flask in the **fume cupboard**.
Add 10 cm³ (0.092 mol, 8.5 g) of *dry* 2-chloro-2-methylpropane (this was prepared in experiment III) to the flask. Also add 10 cm³ (0.094, 8.7 g) of *dry* methylbenzene.
Over about 15 mins, add small portions of the AlCl₃. After each addition, swirl & seal the flask with the cork. Cool the flask with iced water & use the HCl trap as necessary.

continued:

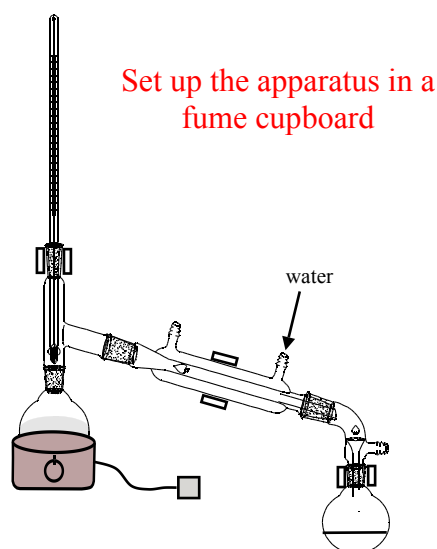
3. When no more HCl is evolved disconnect the trap and add, a little at a time with swirling, about 30 cm³ of iced water to the reaction mixture in the Buchner.



5. Allow the layers to separate and then run off the lower aqueous phase. Discard this down the fume cupboard sink washing away with plenty of water. Wash the organic phase with about 20 cm³ of distilled water discarding as before. Wash the organic layer with about 10 cm³ of 10% sodium carbonate solution (allow for evolution of CO₂ and expansion!). Run off the aqueous layer and discard. Wash the organic layer with 10 cm³ of distilled water & then discard the aqueous layer.

6. Run the organic phase into a small, dry, beaker containing a couple of spatulas of anhydrous sodium sulphate. Stir the mixture from time to time over a period of about 5 minutes. Decant into a small distillation flask (about twice the volume of the organic product). **Note:** It may be convenient for a number of students to combine their products and then distil in a larger apparatus. If this is done it is advisable for each student to weigh his or her product *before* pooling so that overall yields can be estimated!

7. Distil organic product collecting in the range 189 -192°C.



8. Weigh product and store in a labelled glass vial. Calculate % yield.

Obtain & interpret ir (or pmr) spectrum

Note: 5-*t*-butyl-1,3-dimethylbenzene could also be synthesised by this method. *m*-Xylene (1,3-dimethylbenzene) would be used instead of methylbenzene. This substance boils in the range, 195-206°C.

Experiment IV: Friedel-Crafts

Example of Outcomes

Preparation of 4-(methylpropyl)-1-methylbenzene.

Boiling point: 190°C (lit. Value: 193°C)

Maximum yield = 0.092 mol ie, $148 \times 0.092 = 13.6$ g

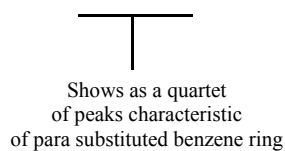
Actual yield = 7.1 g

% yield = $(7.1/13.6) \times 100 = 52\%$

IR: strong to medium peaks at: 3100-2870, 1520, 1459, 1360, 1270, 815, 550 cm^{-1}

Aromatic CH str just above 3000 and aliphatic CH str just below 3000 cm^{-1}

PMR: 1.30, 2.30, 7.10, 7.25 ppm

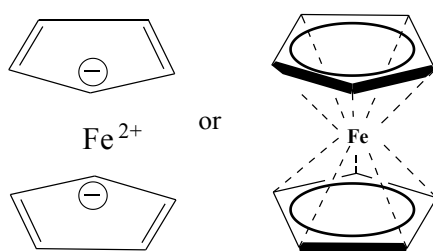


Experiment V

Friedel-Crafts Acylation

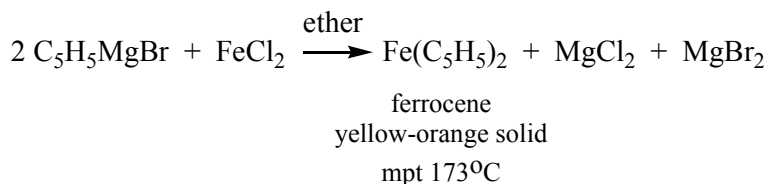
Acetylation of Ferrocene

Ferrocene is an example of an organo-metallic 'sandwich' compound. The molecule consists of an iron(II) ion between two cyclopentadienyl rings. It is, however, a covalent molecule.

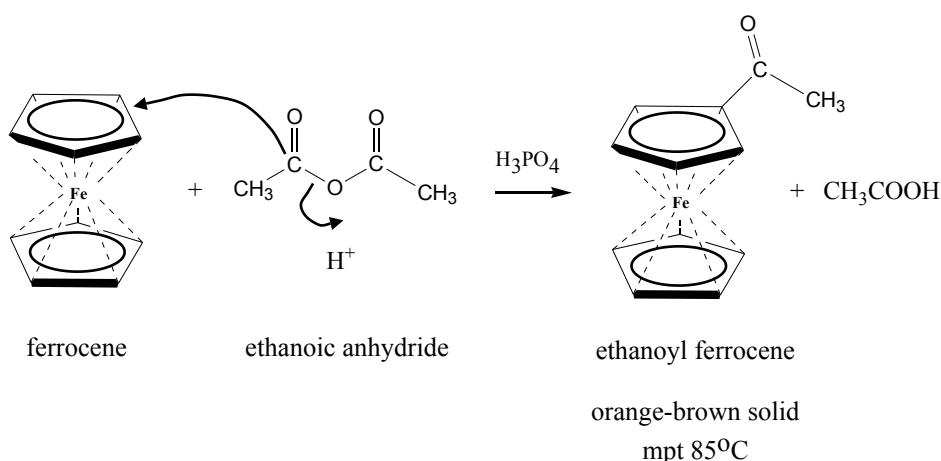


The iron(II) receives a share of 12 electrons from the cyclopentadienyl rings. Giving it the stable Kr electron configuration. The whole molecule is very stable and exhibits aromatic properties.

The molecule was first synthesised by Kealy & Paulson in 1951. They made it by reacting cyclopentadienyl magnesium bromide with iron(II) chloride in ether.

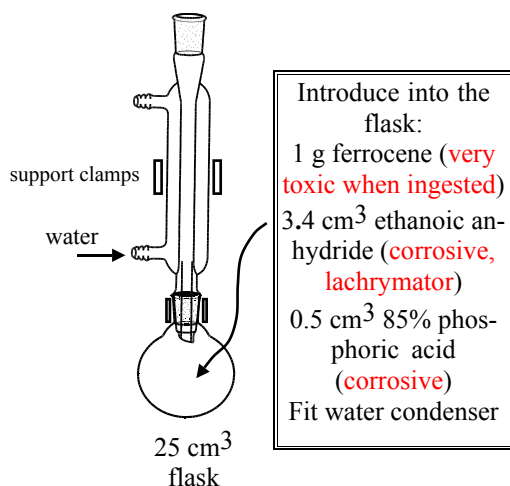


Like benzene and other aromatic species ferrocene undergoes electrophilic substitution reactions. It exhibits the Friedel-Crafts reaction and may be acetylated by reaction with ethanoyl chloride or ethanoic anhydride. Anhydrous aluminium chloride is commonly used as catalyst in this type of reaction, however, since ferrocene is so reactive towards electrophiles milder conditions can be employed. Phosphoric acid may be used in place of aluminium chloride.

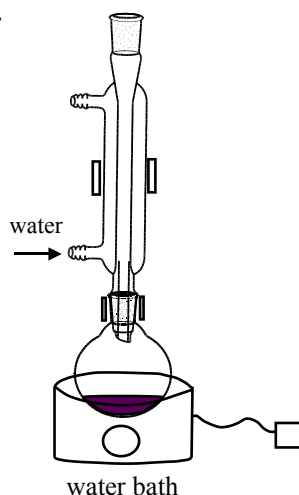


Procedure:

1 Use apparatus and materials in a fume cupboard. Wear safety spectacles and gloves.



2.

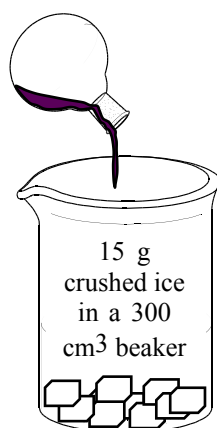


Swirl the contents of the flask.

Heat is generated as the reaction starts up.

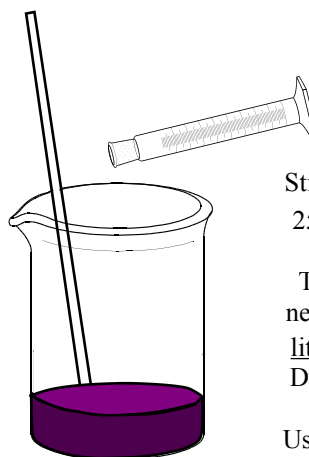
Continue swirling the mixture whilst warming on a water bath. The ferrocene should dissolve and the mixture acquire a darker colour (greenish). Heat more strongly on a hot water bath for about ten minutes. The mixture may develop a purple colour.

3.



Pour the contents of the flask onto crushed ice in a 300 cm³ beaker. Rinse out the flask, into the beaker, with small volumes of ice cold distilled water.

4.



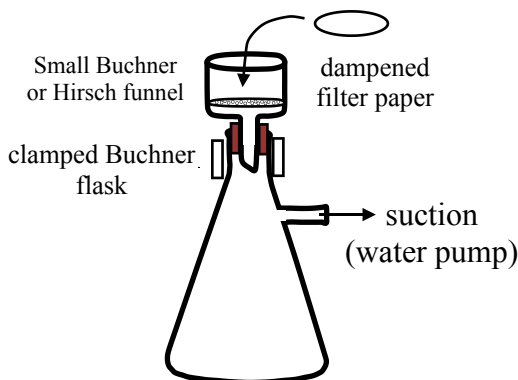
Stirring with a glass rod, carefully add 25 cm³ of 3M NaOH (**CARE: corrosive**).

The mixture should still be acid so neutralise by adding solid NaHCO₃, a little at a time, until neutral to litmus. During this addition foaming will occur. Keep this to a minimum.

Use the glass rod to break up any solid lumps and stir to obtain a brownish suspension.

Allow the mixture to stand for about 15 minutes.

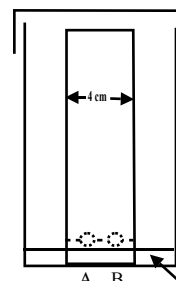
5. **Note:** Like ferrocene, acetyl ferrocene is toxic.



Filter the mixture from 4 using reduced pressure. Suck the crude product as dry as possible and then press dry between layers of paper towel or filter paper (the solid should be an orange-brown colour). Further drying can be achieved by placing the product in a desiccator over silica gel.

Take care not to breathe in any particles of product.

6. (on silica gel plate)



A = small spot of ferrocene solution

B = small spot of crude acetylferrocene solution

Both dilute solutions made up in diethyl ether (**CARE: highly flammable**)

Eluting solvents:

pet. spirit (40-60): absolute ethanol (30:1)
or, pet. spirit (40-60): ether (9:1)
or, toluene: absolute ethanol (30:1)

When the plate has dried you may be able to see the spots due to ferrocene and acetylferrocene. If not, place the plate in a beaker of iodine vapour when the spots should appear brown (perform this in a fume cupboard). Record R_f values.

7. Introduce your crude product into a small conical flask and recrystallise. This may be achieved by dissolving the majority of the product in the minimum of hot hexane. Heat on a water bath in the fume cupboard. Decant the brownish solution, from any insoluble residue, into another clean, small, conical flask and leave to stand. Reddish-brown crystals of acetyl ferrocene will form and can be filtered off and dried. Weigh the sample of recrystallised material & place in a labelled vial. Take its melting point.
Note: The hot hexane solution can be purified further by adding decolourising charcoal and filtering whilst hot. However, this additional step will reduce the yield!
8. Calculate the % yield.

If possible obtain ir and pmr spectra of your product. Compare with spectra of the starting material (ferrocene).

Experiment V

Synthesis of Acetyl Ferrocene

Example of Outcomes

Yield = 0.5 g (0.0022 mol)

Mass of ferrocene used = 1.00 g (0.0054 mol)

% yield = $(0.0022/0.0054) \times 100 = 41 \%$

Melting point of product = 81°C (literature value = 86°C) The recorded mpt indicates that the reaction product contains some impurity. This impurity could be unreacted ferrocene and/or diacetyl ferrocene.

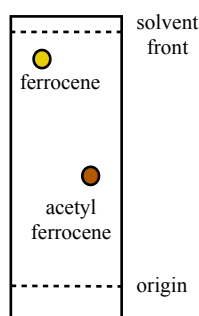
Pmr spectrum: shows 4 sets of peaks corresponding to: 5 protons in the unsubstituted cyclopentadienyl ring (4.20 ppm), 3 protons in the acetyl group (2.40 ppm), 2 protons in the substituted cyclopentadienyl ring adjacent to the acetyl group (4.77 ppm) and 2 protons in the substituted cyclopentadienyl ring remote from the acetyl group (4.50 ppm).

The starting material, ferrocene, shows only one peak at 4.20 ppm.

IR spectrum: Main features: $3000\text{--}3100\text{ cm}^{-1}$ complex group of peaks corresponding to the aromatic protons (small peaks), 1662 cm^{-1} corresponding to the $\text{C}=\text{O}$ in the acetyl group (large peak) and a large peaks at 1470 & 1285 cm^{-1} .

The starting material, ferrocene, does not of course show the large carbonyl absorption at 1662 cm^{-1} or the strong absorptions at 1470 & 1285 cm^{-1} .

TLC

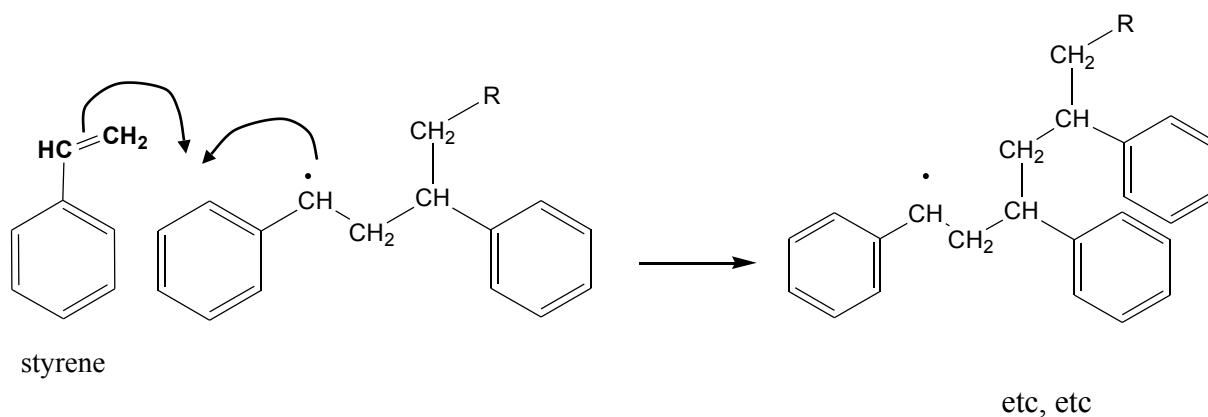
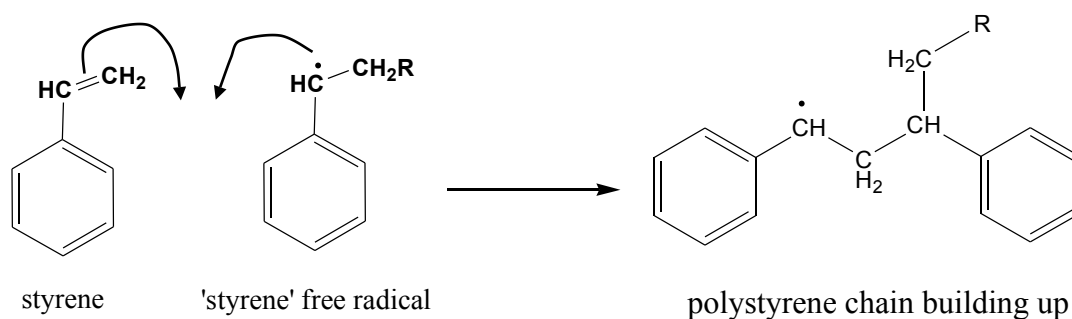
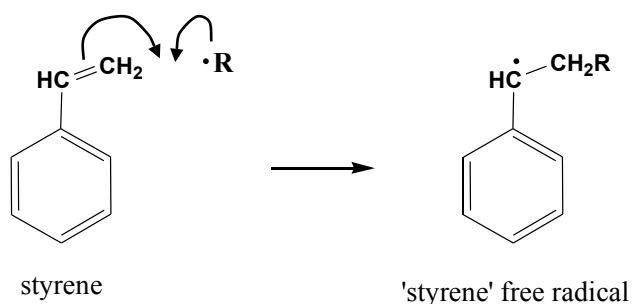
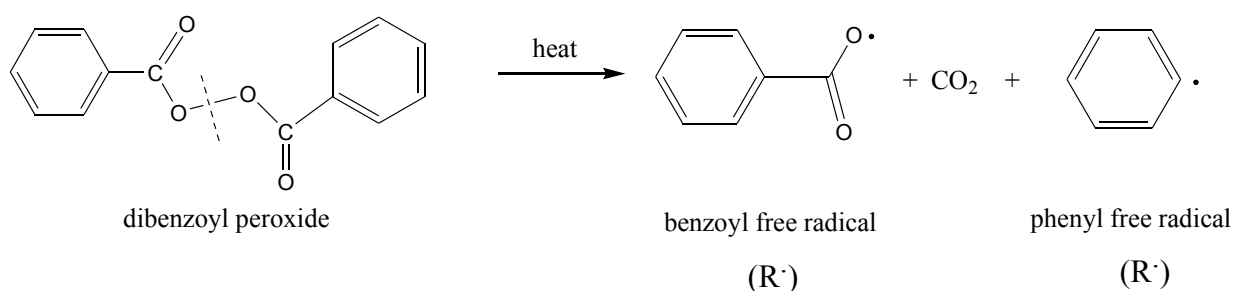


Experiment VI

The Preparation of Polystyrene

Large quantities of polystyrene are used to manufacture foam for insulation. Dibenzoyl peroxide, the free radical generating agent used in this preparation, is used commercially to bleach white flour and as the active ingredient (10%) of a well known cream for treating acne. It is also used in hair bleach and for whitening teeth!

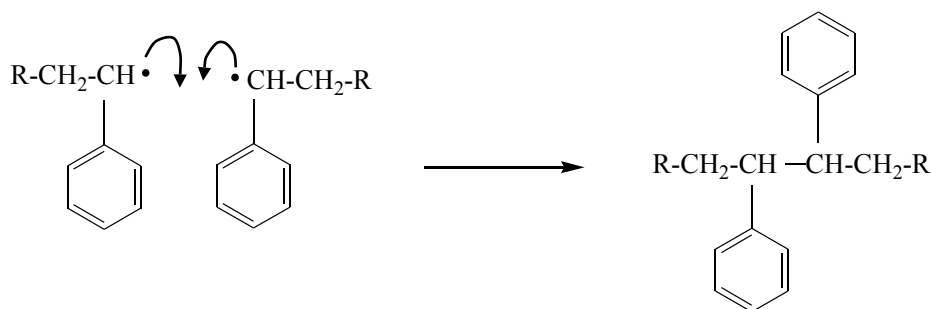
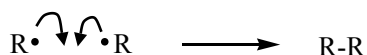
Polymerisation Mechanism:



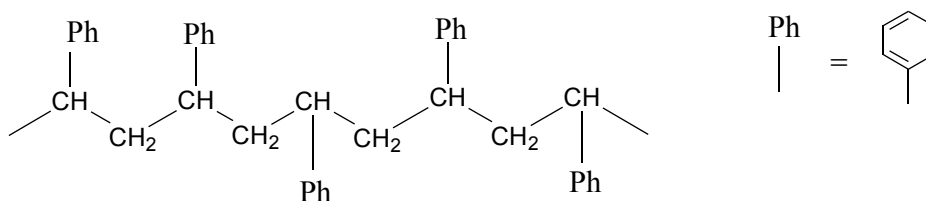
continued:

The reaction is terminated by residual free radicals combining to give neutral species.

eg,



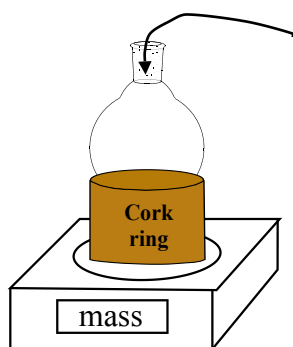
The polystyrene produced in the following experiment has a molecular mass in the range, 2 000 to 40 000, however, polystyrenes with molecular masses up to 100 million have been prepared. Also, the polystyrene from this preparation has an *atactic* (random) arrangement of phenyl groups along the length of the chain.



Procedure: The following operation must be performed in a fume cupboard.

Wear safety spectacles and gloves

1.

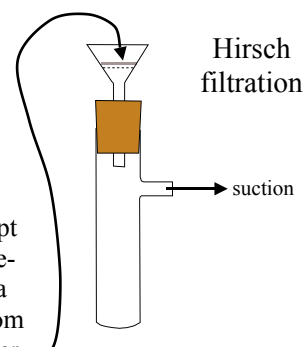


Add 6.5 g (0.063 mol) of styrene. (**CARE: Toxic: harmful to the eyes & to other organs by inhalation or ingestion**).

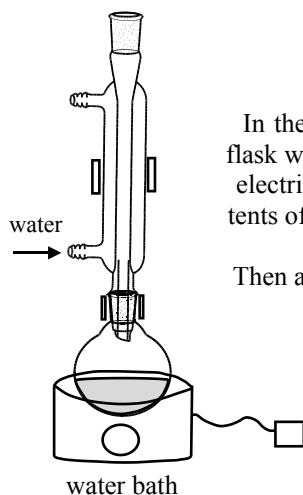
Add approximately 30 cm³ of **dry** methylbenzene (toluene).

Add 0.1 g of dibenzoyl peroxide. (**CARE: Toxic & potentially explosive**)
Add a couple of antibump granules.

This is a white solid kept under water until it is required. Using a spatula take a **small** quantity from the bottle and filter under suction; suck dry on the filter. Weigh some of this into the flask (0.1 g) and return the rest to the storage bottle.



2.



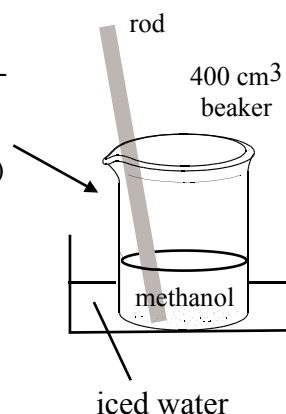
In the fume cupboard, fit the flask with a water condenser and electric heater. Reflux the contents of the flask for 75 minutes.

Then allow the mixture to cool.

3.

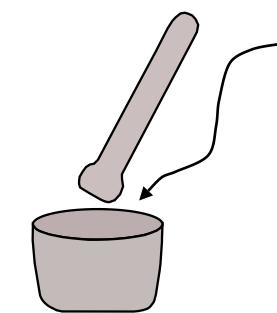
When cool, pour the reaction mixture gradually into 175 cm³ of stirred methanol (**CARE: Toxic**) contained in a beaker. Cool the beaker in iced water.

Polystyrene should form as a white powder; some of it may form as solid with the appearance of chewing gum!



Continued:

4.



small/medium
mortar & pestle

If your product is 'gummy' introduce it into a mortar and triturate (gently squeeze) with a little methanol. During this process the waxy mass will harden and eventually become brittle as the residual methylbenzene is squeezed out of the impure polystyrene.

Filter off the powdered polystyrene, dry on a filter paper at room temperature (or at 30-40°C on a warm, dry, surface), weigh & store in a labelled vial.

5.

Calculate the % yield.

Obtain an ir spectrum and compare with a standard polystyrene spectrum.

Identify the main features.

Experiment VI

The Preparation of Polystyrene

Example of Outcome

Mass of styrene used = 6.5 g

Mass of polystyrene obtained = 1.95 g

% yield = $(1.95/6.5) \times 100 = 30\%$

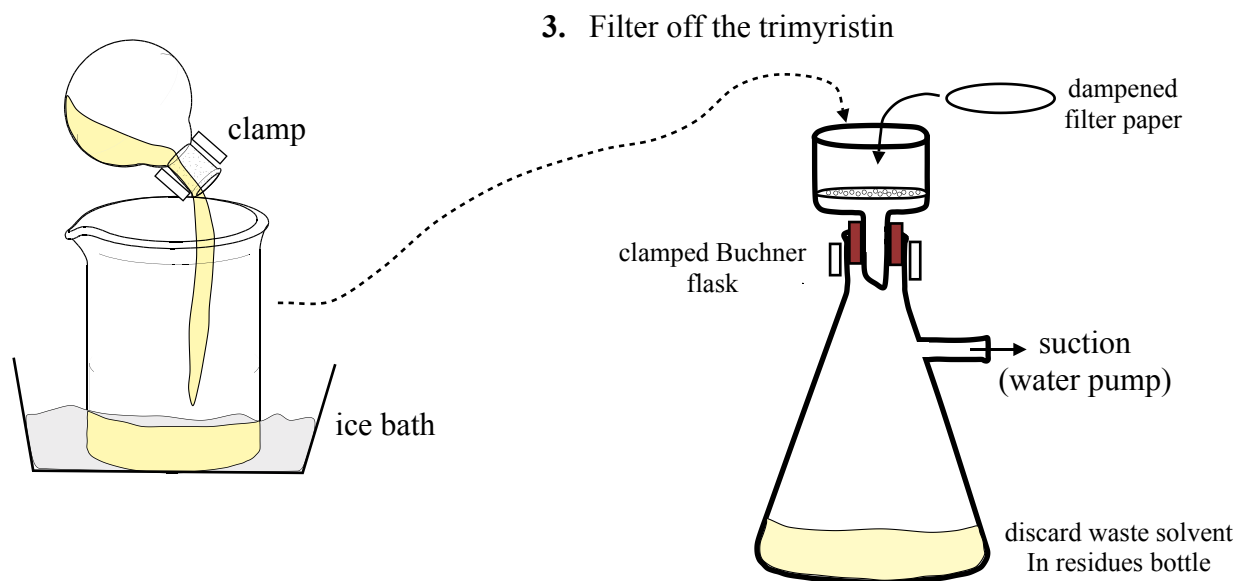
IR spectrum: Dissolved about 0.4g of polystyrene in 1 cm³ of methylbenzene. Poured distilled water into a petri dish until the dish was nearly full. Poured the polystyrene solution onto the surface of the water. Allowed the methylbenzene to evaporate with the dish inside a fume cupboard.

Carefully removed the polystyrene film from the petri dish onto some tissue paper. Allowed the film to dry and then supported a small piece in a holder for ir examination.

The spectrum showed all of the major features of authentic polystyrene. Characteristic absorptions occurred at 2851 (C-H str), 1600 (unsaturation in the aromatic rings) & 906 (CH bending in aromatic rings) cm⁻¹.

continued:

2. Allow the ether to finally syphon into the still, remove the heat source, disconnect the flask and pour the ether solution into 120 cm³ of methanol in a large beaker (do this in the fume cupboard and avoid getting methanol on your skin and do not allow it to splash on your face; methanol is poisonous). Cool the mixture in an ice bath.



4. Recrystallise from 1:1 ether/methanol or propanone. Heat on a water bath in the fume cupboard. (**CARE: flammable, toxic**). Crystallisation, from the recrystallising solvent may be slow! Air dry. Weigh. Calculate % fat in the nutmeg. Measure the melting point of the trimyristin. What would be the outstanding features of the trimyristin infra-red spectrum?

Follow-up exercise: Saponification of Trimyristin.

The ester, trimyristin, can be hydrolysed by heating with alkali (*saponification*).

Introduce 5 g (0.007 mol) of trimyristin into a 100 cm³ round bottomed flask. Add 30 cm³ of 10% potassium hydroxide in industrial methylated spirit (**CARE: Flammable & Corrosive**). Add a few antibump granules and reflux the mixture on an electric heater for 2 hours. Cool the flask and carefully pour the contents into about 60 cm³ of water contained in another round bottomed flask (250 cm³). Make the solution acid to litmus by adding concentrated hydrochloric acid (**CARE: Highly Corrosive**) dropwise with swirling. Fit a condenser, add antibump granules, and reflux for about 15 minutes.

Pour the mixture into a 250 cm³ beaker and cool with iced water. Tetradecanoic acid (myristic acid) solidifies and may be filtered off under suction. Dry (below 45°C) and weigh. The product can be recrystallised from ethanol. Obtain a melting point.

If possible, compare the ir spectrum of myristic acid with that of trimyristin.

Experiment VII

The Extraction of Trimyristin from Nutmeg

Example of Outcomes

Mass of trimyristin obtained = 3.1 g

% trimyristin in the nutmeg = $(3.1/12.0) \times 100 = 26\%$

Melting point extracted trimyristin = 57°C

Main IR features: Large ester carbonyl absorption at 1735 cm^{-1} & intense absorption just below 3000 ($3000 - 2800$) cm^{-1} due to saturated C-H stretching.

Main PMR features: Strong absorption peak at 1.35 ppm due to $(\text{CH}_2)_{10}$ groups and small peaks due to the terminal CH_3 's and the CH_2 's adjacent to carbonyl groups.

Follow-up exercise (Saponification of Trimyristin):

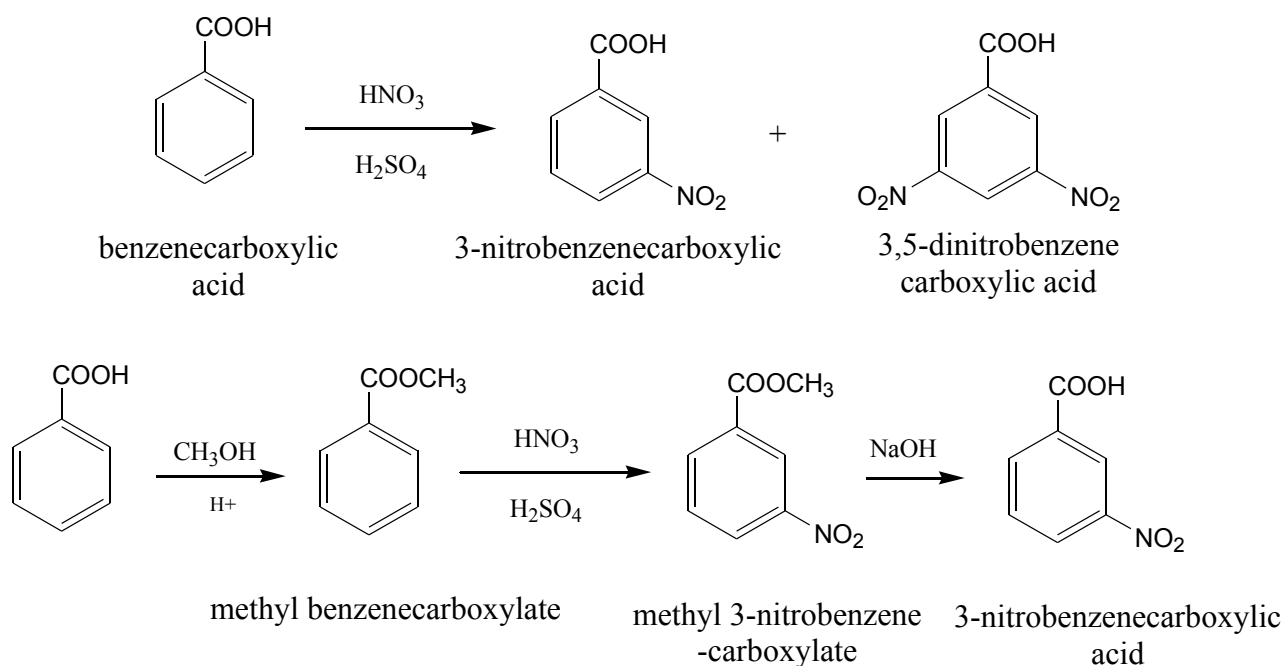
Myristic acid melts in the range, $54-56^{\circ}\text{C}$.

Its ir spectrum shows a series of fairly broad peaks (typical of carboxylic acids). It shows broad absorption in the region of 3400 cm^{-1} due to the OH group (in the COOH function) and also broad absorption at 1730 cm^{-1} due to the carbonyl group (in the COOH function). Trimyristin shows no OH absorption and its its absorption peaks are sharper.

Experiment VIII

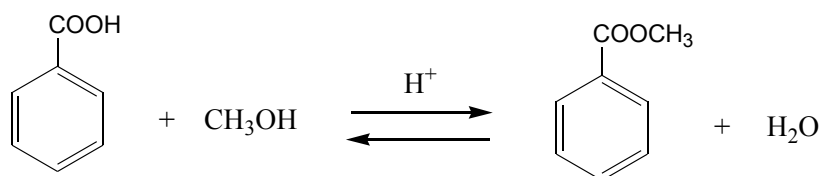
A Multi-step Synthesis: The Synthesis of 3-nitrobenzenecarboxylic acid

Benzenecarboxylic acid can be nitrated with a mixture of concentrated nitric & sulphuric acids. However, a mixture of mono and di-nitro carboxylic acids is produced. More selective nitration is achieved by nitrating the ester, methyl benzenecarboxylate, and then hydrolysing the nitro-ester.

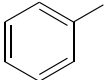


This experiment involves esterification of benzenecarboxylic acid, nitration of the ester and then saponification to give the required product. Methyl benzenecarboxylate is a liquid and must be isolated by distillation. The nitro-ester and nitro-acid are both crystalline solids and must be purified by recrystallisation.

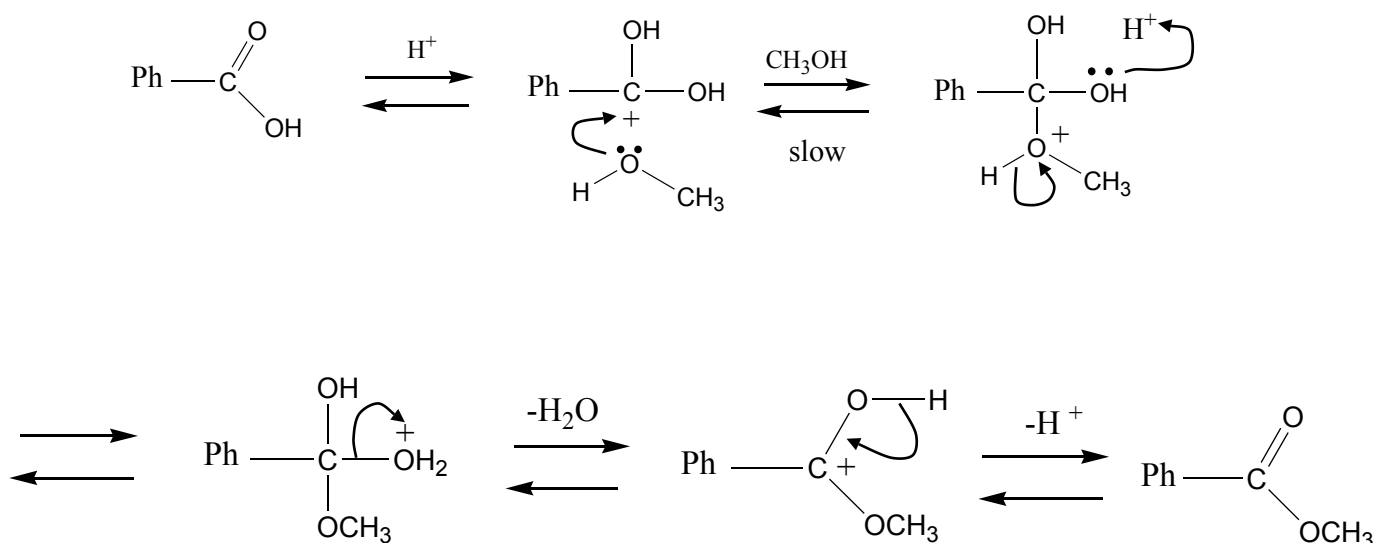
Step one: Esterification



Mechanism:

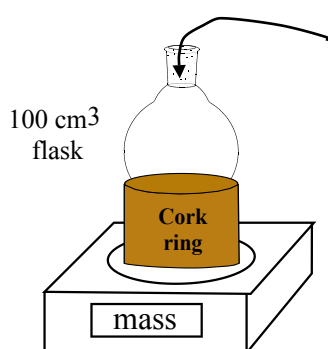
Let  be represented, Ph
phenyl group

continued:



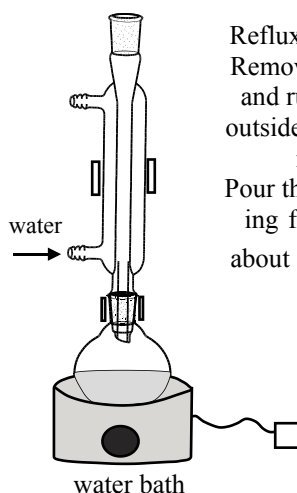
Procedure:

1.



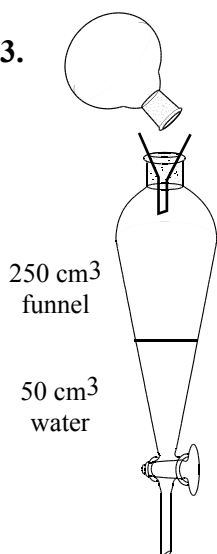
12.2 g (0.1 mol) benzenecarboxylic acid.
25 cm³ methanol (19.7 g, 0.62 mol **CARE: Toxic**).
3 cm³ concentrated sulphuric acid added **slowly** with swirling of the flask.
3 or 4 antibump granules.

2.



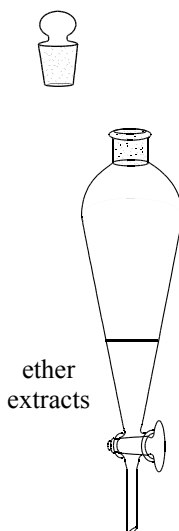
Reflux gently for 45 minutes. Remove from the heat source and run cold water over the outside of the flask to cool the reaction mixture. Pour the mixture into a separating funnel which contains about 50 cm³ of distilled water

3.



Rinse the flask into the funnel with about 25 cm³ of diethyl ether (**CARE: Highly flammable**). Mix the contents of the funnel, carefully, allowing for expansion. Run off the aqueous layer into a beaker. Run off the ether layer into another beaker. Re-introduce the aqueous layer into the funnel and extract with a further 10 cm³ of ether. Combine the ether extracts. Discard the aqueous layer down the fume cupboard sink washing away with plenty of water.

4.



Wash the ether extracts, first with distilled water (about 20 cm³) then with 5% sodium carbonate solution (about 25 cm³. **CARE:** allow for expansion as CO₂ is evolved).

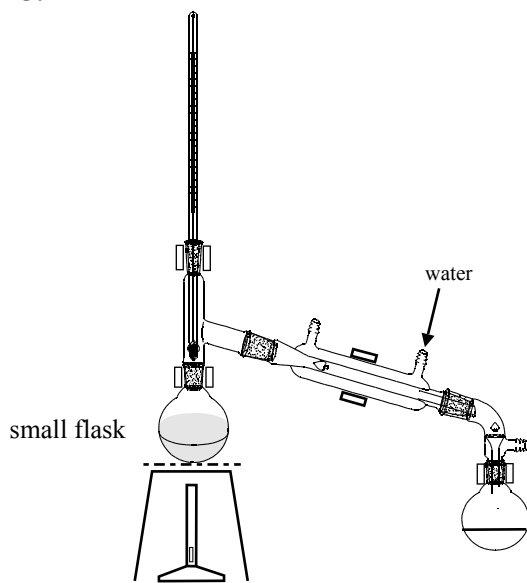
Isolate the ether solution into a clean beaker and add a couple of spatulas of anhydrous sodium sulphate drying agent. Leave for 10 mins with occasional swirling.

Decant the dry ether into another dry beaker (washing the drying agent as necessary with fresh ether). In a fume cupboard, evaporate the ether on a water bath.

When all of the ether has evaporated, pipette the ester into a previously weighed round bottomed flask. Choose a flask so that it is about one third full with ester. Weigh flask plus ester. Add a couple of antibump granules.

continued:

5.



Make sure all of the ether has been evaporated.

Distil collecting above 190°C into a previously weighed flask or sample bottle.

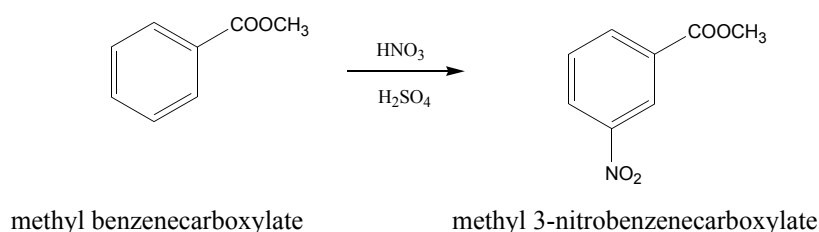
Note the mean distillation temperature.

Calculate % yield (based on benzenecarboxylic acid used).

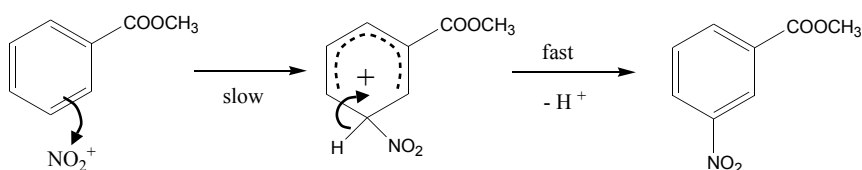
Store in properly labelled vial.

Obtain an ir spectrum of the purified ester & identify the main features which indicate that the synthesis has been successful.

Stage Two: Preparation of Methyl 3-nitrobenzenecarboxylate.

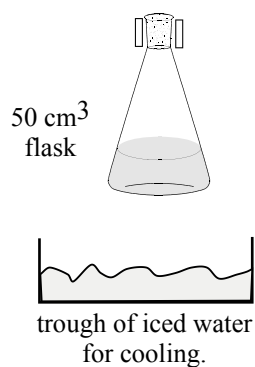


mechanism:



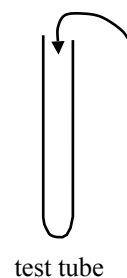
Procedure:

1.



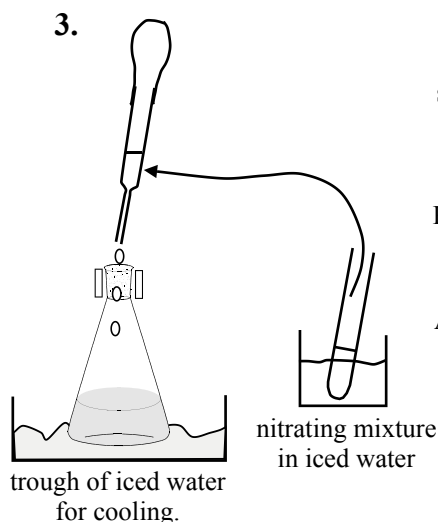
Weigh into the flask 2.0 g of methyl benzenecarboxylate. Add 4 cm³ of concentrated sulphuric acid slowly with swirling (**CARE: concentrated sulphuric acid is very corrosive to the skin; in the event of skin contact wash the affected area with copious amounts of cold water**) Cool this mixture by partially immersing the flask in iced water in a plastic trough.

2.

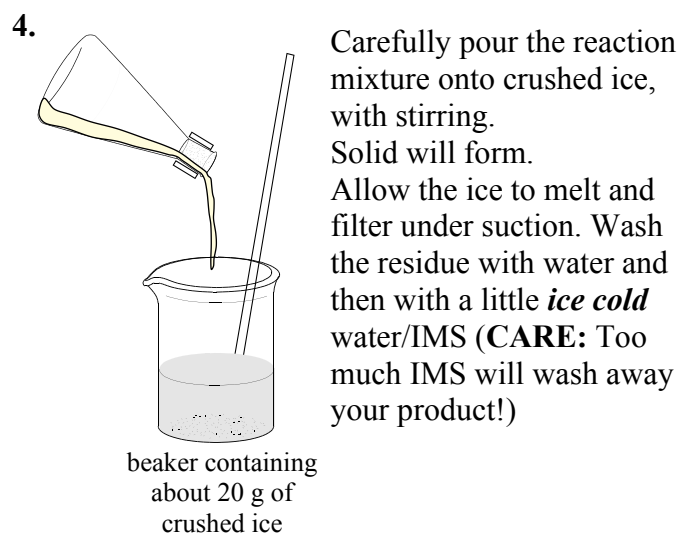


Introduce 1.5 cm³ of concentrated nitric acid. Add slowly with stirring, 1.5 cm³ of concentrated sulphuric acid. Cool this mixture by supporting the tube in iced water. This is the **nitrating mixture**.

continued:

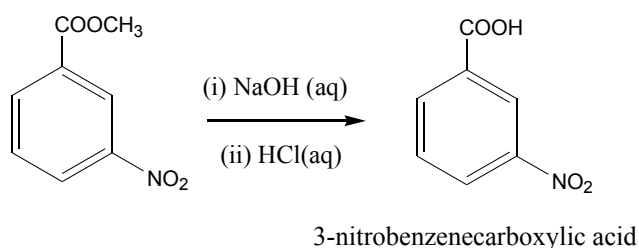


Add the nitrating mixture slowly (over about 15 minutes) to the contents of the flask. Stir the reaction as this addition is made. Keep the temperature of the reaction mixture in the range 0-6°C. After the addition allow the flask, containing the reaction mixture, to stand at room temperature for 15 minutes.

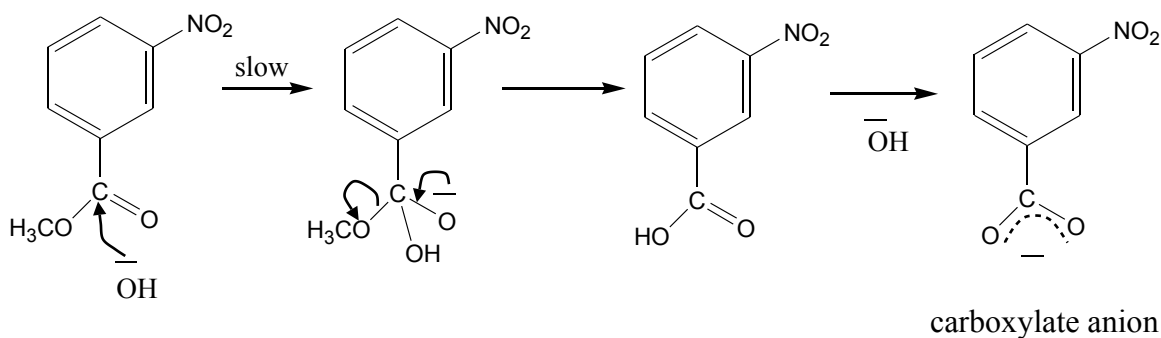


5. Recrystallise the crude nitro ester from IMS (10-15 cm³). Filter under suction and air or oven dry (below 50°C!). Weigh your product and calculate % yield. Measure the melting point. Obtain an ir spectrum and identify the main features.

Stage Three: Preparation of 3-nitrobenzenecarboxylic acid



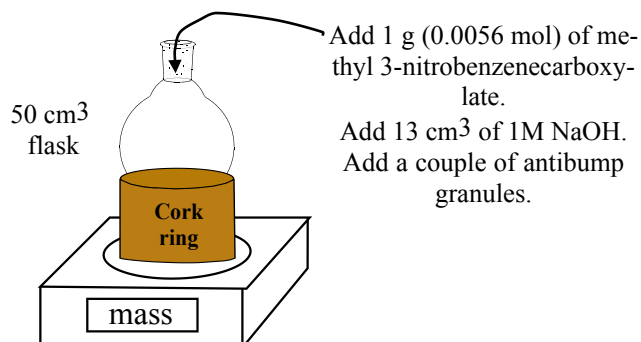
Mechanism:



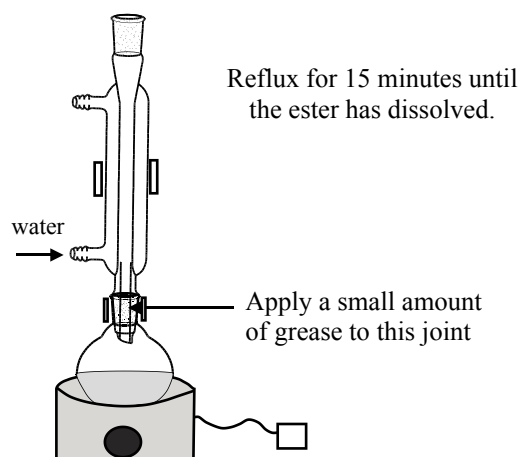
The carboxylate anion is converted to the free acid by treatment with dilute mineral acid in the final stage of the preparation.

Procedure:

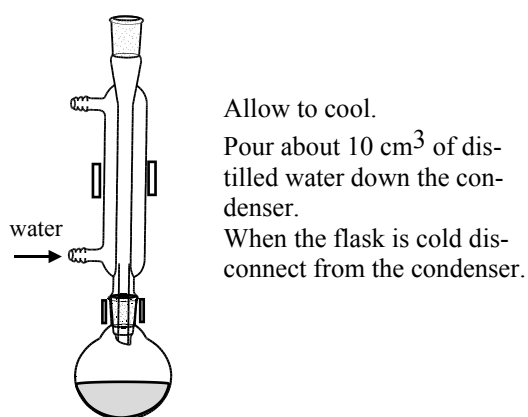
1.



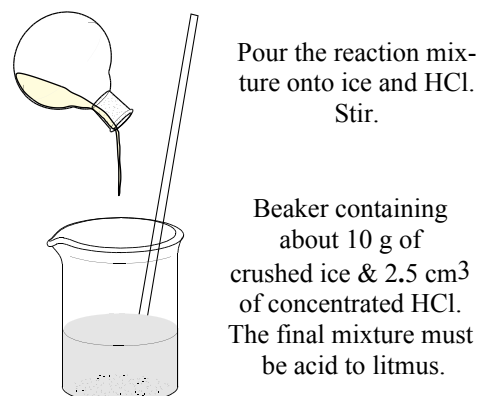
2.



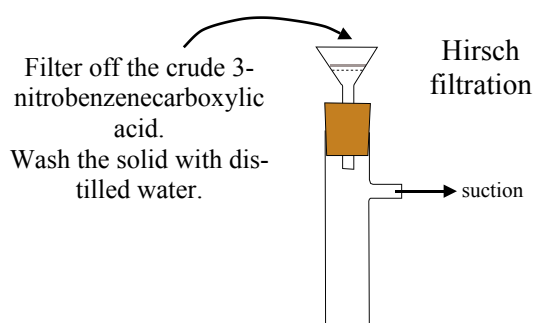
3.



4.



5.



6.

Recrystallise the carboxylic acid from the minimum of 0.3M hydrochloric acid.

Dry in the oven at about 60°C.
Weigh and calculate % yield.
Measure the melting point.

Obtain an ir spectrum and identify the structural features indicated.

Experiment VIII

A Multistep Synthesis

The Synthesis of 3-nitrobenzenecarboxylic acid.

Example of Outcomes

Step One: Preparation of Methyl benzenecarboxylate.

Mass of methyl benzenecarboxylate obtained: 6.5 g (0.048 mol)

% yield = $(0.048/0.10) \times 100 = 48\%$ (This is rather low. Product was lost during the isolation and purification stages)

Boiling point (mean) = 192°C . (lit. Value 199°C)

IR spectroscopy: The product showed intense absorption at 1720 cm^{-1} due to the ester carbonyl and no absorption in the region $4000 - 3100\text{ cm}^{-1}$ due to carboxyl group.

Pleasant smelling liquid (floral/cherry odour). Niobe oil.

PMR spectrum (in CDCl_3): Shows a nice singlet due to methyl protons (in COOCH_3 group) and two complex bands in the aromatic region at 7.40 & 8.02 ppm.

Step Two: Preparation of 3-nitrobenzenecarboxylate.

Mass of nitro product obtained = 1.80 g (0.0099 mol)

% yield = $(0.0099/0.0147) \times 100 = 67\%$

Melting point of product = 77°C

IR spectroscopy: showed absorption due to the nitro group in the regions, 1560-1490, 1360-1340, 620-480 cm^{-1} .

Step Three: Preparation of 3-nitrobenzenecarboxylic acid.

Mass of 3-nitrobenzenecarboxylic acid = 0.60 g (0.0036)

% yield = $(0.0036/0.0056) \times 100 = 64\%$

Melting point = 138°C (lit vale 141°C)

IR spectroscopy: (KBr disc) Broad intense absorption in the range, 3600 - 2300 cm^{-1} characteristic of COOH . Acid carbonyl at 1680 cm^{-1} and nitro absorptions at 1520 and 1340 cm^{-1} .

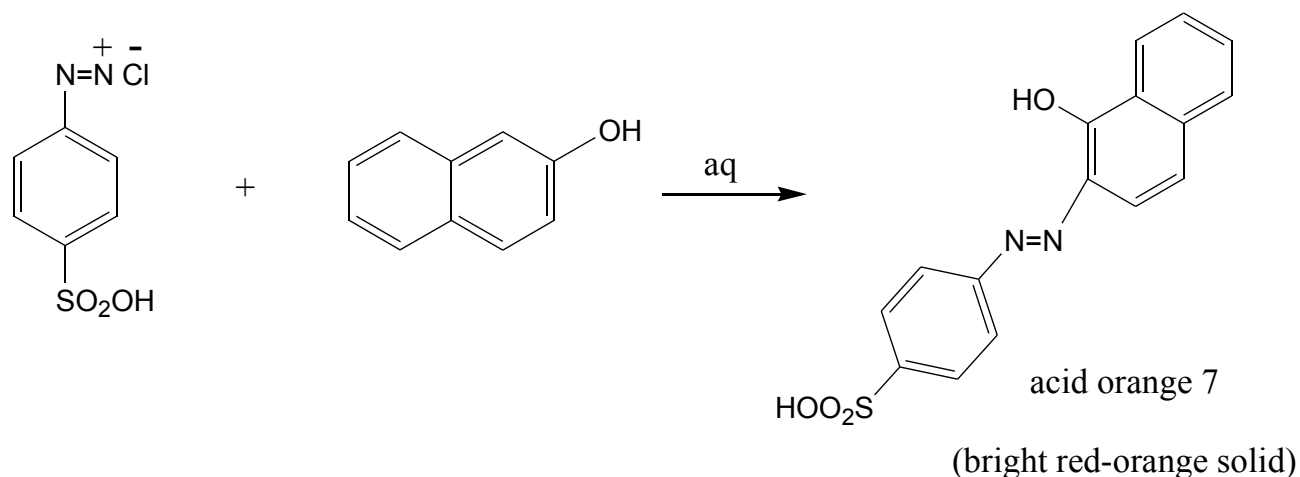
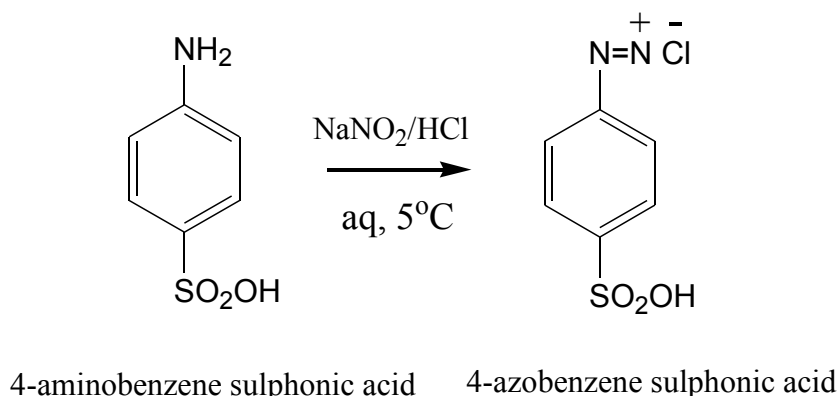
PMR spectrum (CDCl_3): broad singlet at 11.67 (due to COOH proton), singlet at 8.96 (due to the aromatic proton between the carboxyl group & the nitro group), & complex bands at 7.74, 8.47 and 8.50 ppm (due to the remaining aromatic protons).

Experiment IX

Preparation of an Azo Dye

4-(2-hydroxy-1-naphthylazo)-benzene sulphonic acid

(also known as, naphthalene orange G, orange II and acid orange 7)



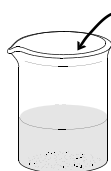
Procedure:

This preparation involves the formation of a diazonium salt. These are liable to explode if allowed to dry out. It is important, therefore, that surplus reagents or filtrates are washed down the fume cupboard sink in running water immediately.

Skin contact with all reagents should be avoided. It is advisable to wear safety spectacles and gloves. In the event of accidental contact wash with plenty of water or soap and water.

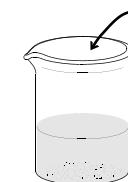
1.

100 cm³
beaker



Dissolve 1 g naphthalen-2-ol in 4 cm³ 2M NaOH (**CARE: Corrosive**) and 10 cm³ of water. **Gently** warm, if necessary, to dissolve solid (do not over-heat).

2.



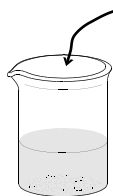
trough of freezing mixture
for cooling.

Stir in 0.5 g anhydrous Na₂CO₃.
Cool mixture by partially immersing the beaker in a freezing mixture (water-ice-salt)

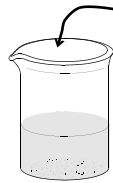
continued:

3. In a **second** beaker,
1.2 g 4-aminobenzenesulphonic acid (sulphanilic acid)
7 cm³ distilled water.
Just sufficient 2M NaOH to make alkaline to litmus.

100 cm³ beaker



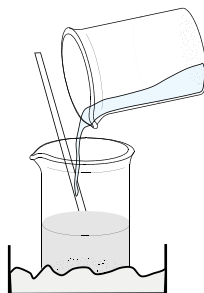
4. Add 10-15 cm³ of crushed ice.
Stir in 2.2 cm³ of concentrated HCl (**CARE: Corrosive & fumes in moist air**) to re-precipitate the aminobenzenesulphonic acid.



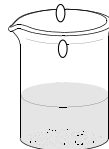
5. Add 0.5 g of sodium nitrate(III) (sodium nitrite) to 5 cm³ of distilled water.



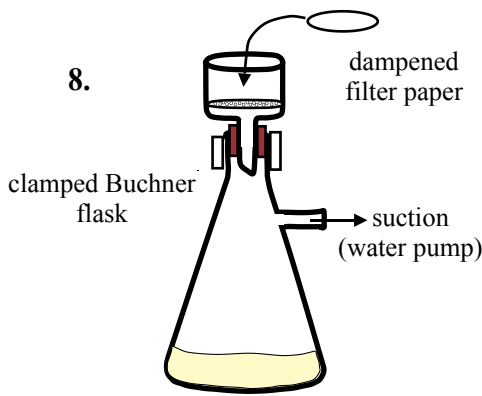
7. Stir the diazotised 4-aminobenzenesulphonic acid carefully (may be some frothing) into the naphthalen-2-ol solution (prepared earlier, 1 & 2). Keep the latter in the ice bath. Stir for a few minutes.



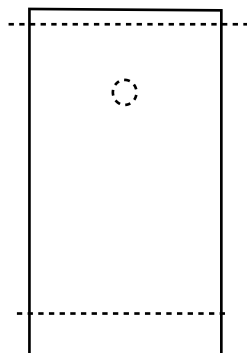
6. Add the NaNO₂ solution to the ice cold aminobenzenesulphonic acid mixture (3 & 4) with stirring. The beaker now contains diazotised 4-aminobenzenesulphonic acid.



8. Filter off the dye under suction. Slowly oven dry at 80°C or in a suitable desiccator. Weigh the dry product. Store in a properly labelled vial. Calculate the % yield.



9. TLC: (set up in fume cupboard)
Silica gel plate.
Eluting solvent: butan-1-ol:
IMS: water: glacial acetic acid (120:20:40:1 cm³)
Judge purity from the number of spots on the developed plate.
Record R_f value of major spot.

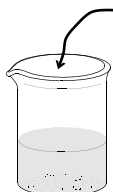


Could also try **reverse phase** tlc:
Tlc plate prepared by immersing in 10% paraffin oil in ether (**CARE: Highly flammable**) and air drying.
Elute with 1:1 IMS:water.
Record R_f value.

10. Use the dye to dye wool.

0.1 g of dye.
100 cm³ distilled water.
Half a spatula of Na₂SO₄.
3 drops of concentrated HCl.
Mix.

250 cm³ beaker



11. Squeeze small piece (say 4 x 4 cm) of undyed woolen cloth in water containing a drop of detergent. Place the material in the dye solution and heat gently (do not boil) for about half an hour. Using tongs, remove the wool, rinse in soapy water and then under the tap. Dry & mount in report.

Experiment IX

Preparation of an Azo Dye

4-(2-hydroxy-1-naphthylazo)-benzene sulphonic acid (also known as, naphthalene orange G, orange II and acid orange 7)

Expected Outcomes

Dye: max yield = 2.25 g (0.00694 mol)

Actual yield = 1.4 g (0.00432 mol)

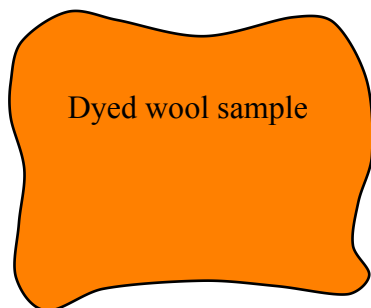
% yield = $(1.4/2.25) \times 100 = 62\%$

Dye decomposes at about 300°C.

Tlc:

Standard phase: $R_f = 0.85$

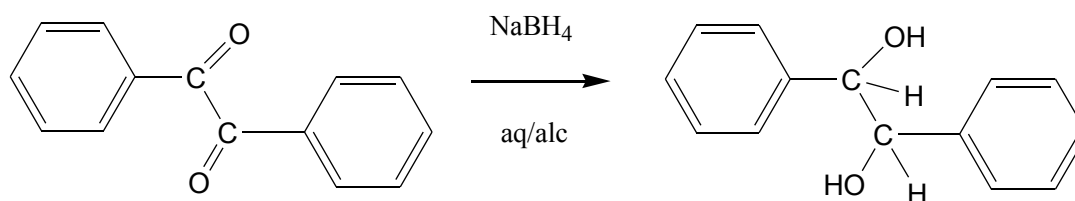
Reverse phase: $R_f = 0.80$



Dyed wool sample

Experiment X

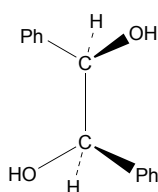
Reduction of a Carbonyl compound using Sodium borohydride



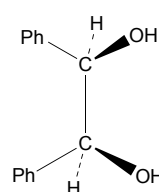
diphenylethanedione
(benzil)

(yellow, mpt 95°C)

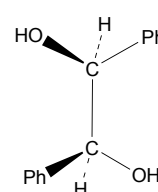
1,2-diphenylethane-1,2-diol
(hydrobenzoin)
(colourless)



R,R-(+)
mpt 148°C



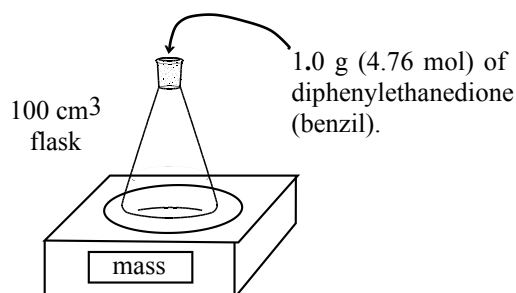
R,S-(meso)
mpt 138°C



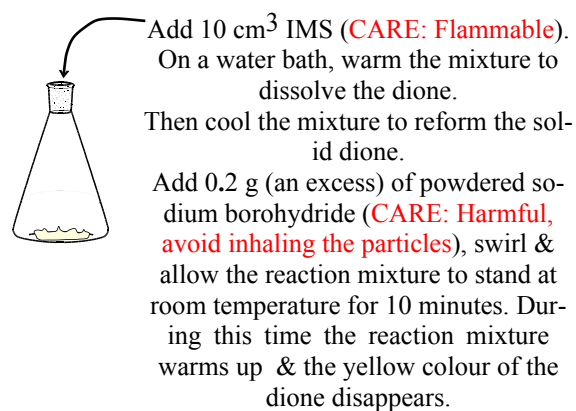
S,S-(-)
mpt 148°C

Procedure:

1.

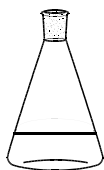


2.



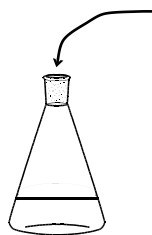
continued:

3.



Add 7 cm³ of distilled water. Heat carefully on a water bath. Gradually raise the temperature of the water bath so that the reaction mixture is *nearly* boiling. The purpose of this is to destroy excess hydride.

4.



Add more distilled water (about 10 cm³) and cool the mixture in iced water.

Isolate the white solid by suction filtration.

Dry the solid on a large watch glass on a warm water bath.

Weigh the dry material and store in a properly labelled vial.

Calculate the % yield based on the amount of diphenylethanedione used.

5.

Measure the melting point of the final product (1,2-diphenylethane-1,2-diol). Compare this with literature values for the various stereoisomers and decide on the most likely structure of your product. Obtain an ir spectrum and identify the main features.

Try writing a reaction mechanism which correlates with the structure obtained.

Experiment X

Reduction of a Carbonyl compound using Sodium borohydride

Example of Outcomes

Maximum yield based on diphenylethanedione used = 1.01 g

Yield obtained = 0.51 g

% yield = $(0.51/1.01) \times 100 = 50.0\%$ (rather a low yield - material lost in work up)

Melting point of product = 140.0°C

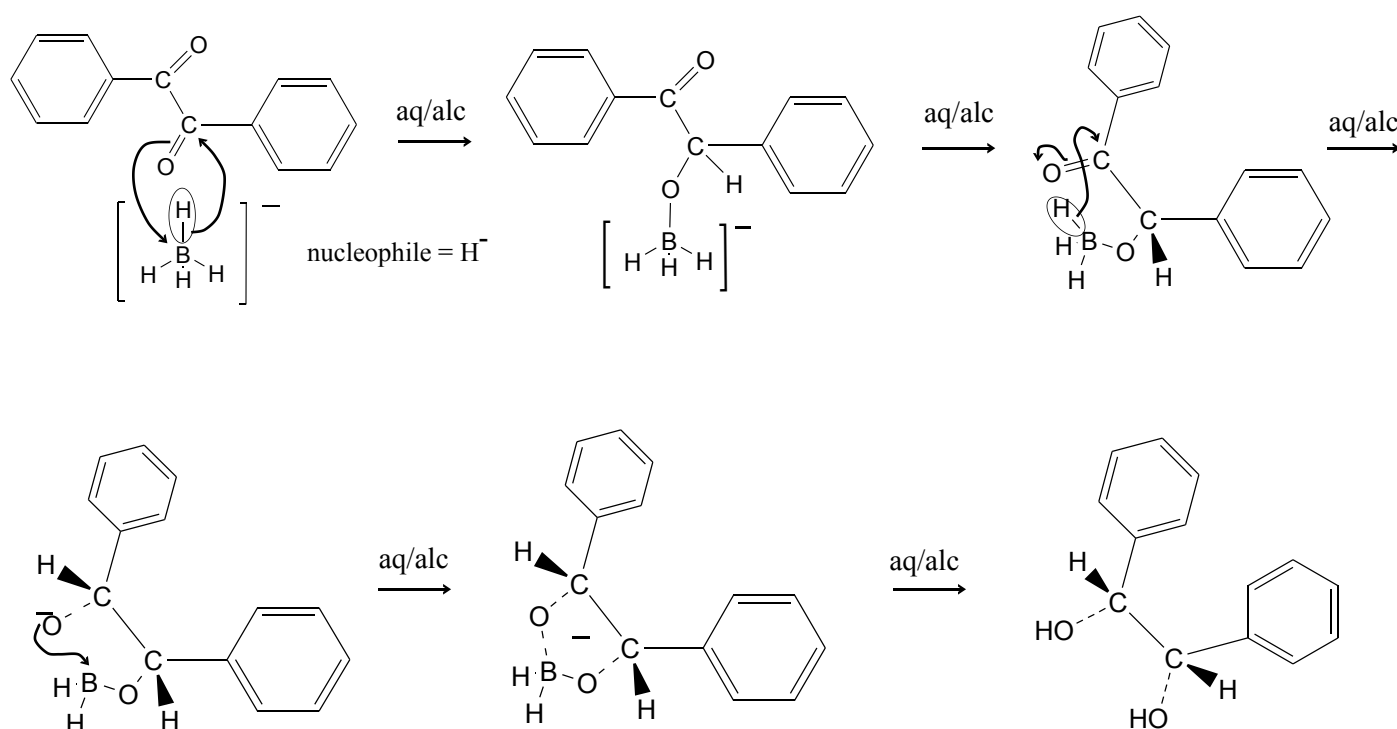
This corresponds most closely to the meso form (other workers have obtained the same result).

(Note: the racemate (+/-) melts at about 120°C)

IR spectrum (KBr disc): this shows a broad, double, peak centred at 3310 cm^{-1} due to the OH groups. Significantly, little or no absorption at 1700 cm^{-1} which indicates that the product is free of the starting material (ie, the di-one). There is a sharp peak at 2880 cm^{-1} due to C-H stretching and small peaks just above 3000 cm^{-1} due to aromatic C-H stretch. Bending vibrations occur in the fingerprint region (eg, 1430 , 1270 , 1040 , 740 cm^{-1}). This correlates well with the expected 1,2-diphenylethane-1,2-diol.

Mechanism:

The following is a suggested mechanism to account for the observed meso product



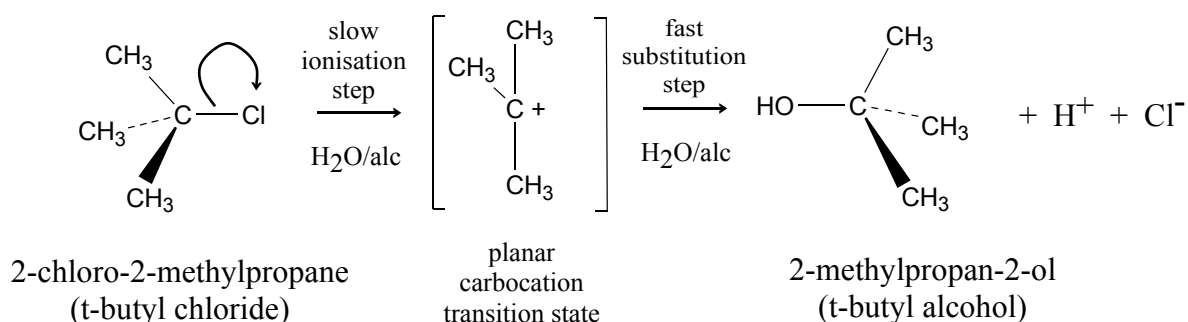
Experiment XI

Kinetics

Hydrolysis of 2-chloro-2-methylpropane (*t*-butyl chloride)

Tertiary halogenoalkanes are readily converted to the corresponding alcohol by warming with alkali. The hydrolysis occurs by first order kinetics involving a slow ionisation step followed by fast nucleophilic substitution in the second non rate determining step.

In aqueous-alcoholic solution at room temperature the hydrolysis occurs more slowly and can be monitored titrimetrically.



$$\text{rate} = k [\text{t-butyl chloride}]$$

$$\& \quad - \frac{d [\text{t-butyl chloride}]}{dt} = + \frac{d[\text{H}^+]}{dt} = k [\text{t-butyl chloride}]$$

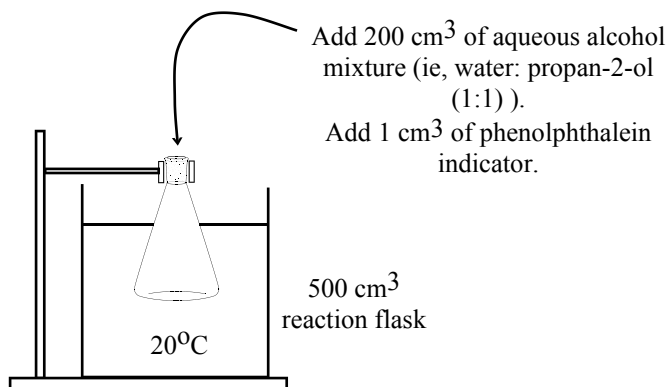
Procedure:

Outline:

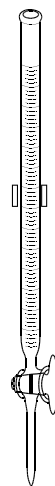
A 1.0 cm³ aliquot of standard sodium hydroxide solution is added to a large volume of the solvent at constant temperature. The solvent contains phenolphthalein indicator. At this stage the mixture is pink due to the indicator in alkaline solution. Halogenoalkane (1 cm³) is added to the reaction vessel and a stop clock is started immediately. The time taken for the colour to fade to colourless, as liberated hydrogen ion neutralises the alkali, is recorded & immediately a further aliquot of alkali is added. Again, the time, at which the mixture becomes colourless, is noted. This process is repeated over a period of about ten minutes & then finally after about two hours by which time the reaction should have finished.

continued:

1.



2.



Introduce sodium hydroxide solution (0.25 M) into a 50 cm³ burette; adjust the level to 0.00. Into the reaction flask, run 1.00 cm³ (V_t) of the alkali. Swirl flask.

The contents will be pink.

3.

Using another, small, burette (or a suitable pipette) add 1.00 cm³ of t-butyl chloride (**CARE: volatile, flammable**) to the reaction flask and **start the stop clock**. Swirl the flask to thoroughly mix.

Observe the reaction mixture closely and when the pink colour disappears record the time (t seconds) and immediately add a further 1.00 cm³ of alkali.

Again, observe the mixture and when the pink colour has faded record the time and add another 1 cm³ of alkali. Continue repeating this process until at least 10 additions of alkali have been made. At each addition record the time. Note the amount of alkali added at this stage.

Tabulate the results.

4.

Take a final reading after about 2 hours (or at the beginning of the next practical period having kept the reaction mixture in a sealed container in the fume cupboard). The total alkali added = V_{inf}

5. For a first order reaction,

$$\ln(a-x) = -k t + \ln a$$

where a = initial amount of reactant and x = amount of reactant used up.

$(a-x)$ = amount of reactant remaining at time t .

A plot of $\ln(a-x)$ against t gives a straight line where the slope = k (rate constant).

In this experiment the volume of alkali used at time t , V_t , is proportional to x and the final volume of alkali, V_{inf} , is proportional to a so $\ln(V_{inf} - V_t)$ can be plotted against time (t) to show the straight line relationship and confirm that the hydrolysis is first order with respect to the halogenoalkane.

From the slope of the graph obtain a value for k (rate constant).

Experiment XI

Kinetics

Hydrolysis of 2-chloro-2-methylpropane (*t*-butyl chloride)

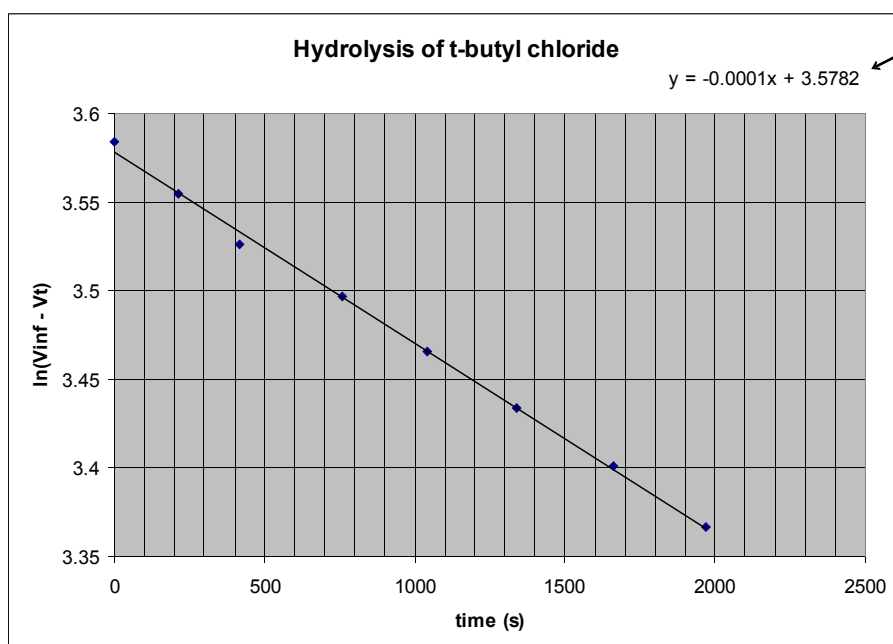
Example of Outcomes

Results:

Vol. NaOH solution cm ³ (V _t)	1.00	2.00	3.00	4.00	5.00	6.00	7.00	36.00
Time (t) secs	215	415	761	1042	1337	1660	1970	∞

Time (t secs)	(V _{inf} - V _t) cm ³	ln(V _{inf} -V _t)
0	36.00	3.584
215	35.00	3.555
415	34.00	3.526
761	33.00	3.497
1042	32.00	3.466
1337	31.00	3.434
1660	30.00	3.401
1970	29.00	3.367

Graphical:



equation of the line

k (rate constant) =
 $1.0 \times 10^{-4} \text{ s}^{-1}$
at 20°C

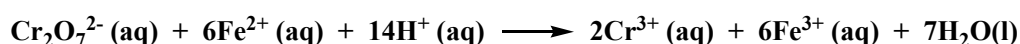
The straight line confirms the first order nature of the hydrolysis and supports the mechanism in which the slow, rate determining step, is the first step in which the halide ionises to form the carbocation transition state. The rate is zero order with respect to the water.

Experiment XII

Potentiometric Redox Titration

Estimation of Iron(II) by titration against Standard Dichromate solution

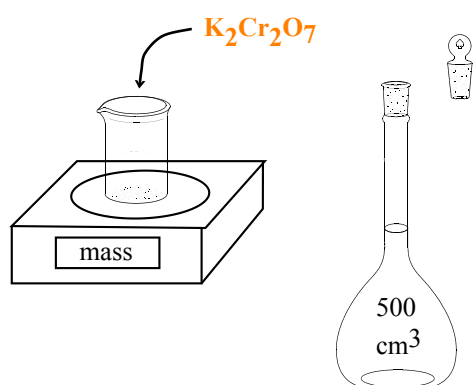
Iron(II) reacts with dichromate according to the following equation:



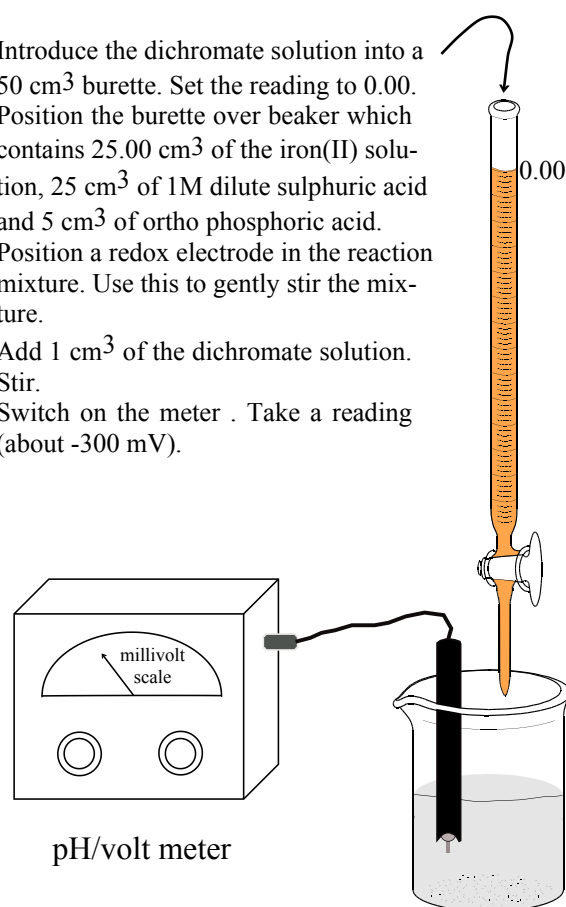
In this experiment standard dichromate solution is titrated against an acidified solution of iron(II) (ie, dilute ammonium iron(II) sulphate). As the iron(II) is oxidised to iron(III) the measured emf changes. This emf is measured, using a redox electrode and high resistance voltmeter (which is a basic pH/volt meter), as known amounts of dichromate solution are added. Emf values are plotted against volume of dichromate solution to give a titration curve from which the end point of the titration can be deduced and the concentration of the iron(II) solution calculated..

Procedure:

1. Prepare a standard solution of potassium dichromate. Prepare 500 cm³ of approximately 0.017 M solution.
The relative molecular mass of potassium dichromate is 294.19.



2. Introduce the dichromate solution into a 50 cm³ burette. Set the reading to 0.00. Position the burette over beaker which contains 25.00 cm³ of the iron(II) solution, 25 cm³ of 1M dilute sulphuric acid and 5 cm³ of ortho phosphoric acid. Position a redox electrode in the reaction mixture. Use this to gently stir the mixture.
Add 1 cm³ of the dichromate solution. Stir.
Switch on the meter. Take a reading (about -300 mV).



continued:

3. Continue titrating the iron(II) solution with dichromate solution. Run in dichromate solution until the emf increases by 20mV. Record both the meter and the burette readings. Add another aliquot of dichromate so that the emf increases by another 20mV and record meter and burette readings. Proceed in this manner until you notice that quite small additions of dichromate provide a 20mV change. This indicates that the end point is approaching. At this stage add the dichromate in small volumes so as not to overshoot the end point. After the end point, larger volumes of dichromate will be required to achieve the 20mV change. Continue adding dichromate, and recording burette and meter readings, until the burette reads 50.00 cm³.

Plot graphs of, (i) mV versus volume of dichromate and (ii) $\Delta mV/\Delta \text{Volume}$ versus volume of dichromate (ie, first derivative curve). From these plots deduce the end point of the titration.

Calculate the molarity of the iron(II) solution.

What is the purpose of phosphoric acid included in the reaction mixture?

Experiment XII

Potentiometric Redox Titration

Estimation of Iron(II) by titration against Standard Dichromate solution

Example of Outcomes

Preparation of Standard Dichromate solution:

Relative molecular mass of potassium dichromate = 294.1

Required: A dichromate solution of concentration = 0.017 M

Mass of potassium dichromate required to make 1 litre of 0.017 M = $0.017 \times 294.1 = 4.9997$ g

Therefore, mass required to make $500 \text{ cm}^3 = 4.9997/2 = 2.50$ g

This amount was weighed out and made up to 500 cm^3 with distilled water.

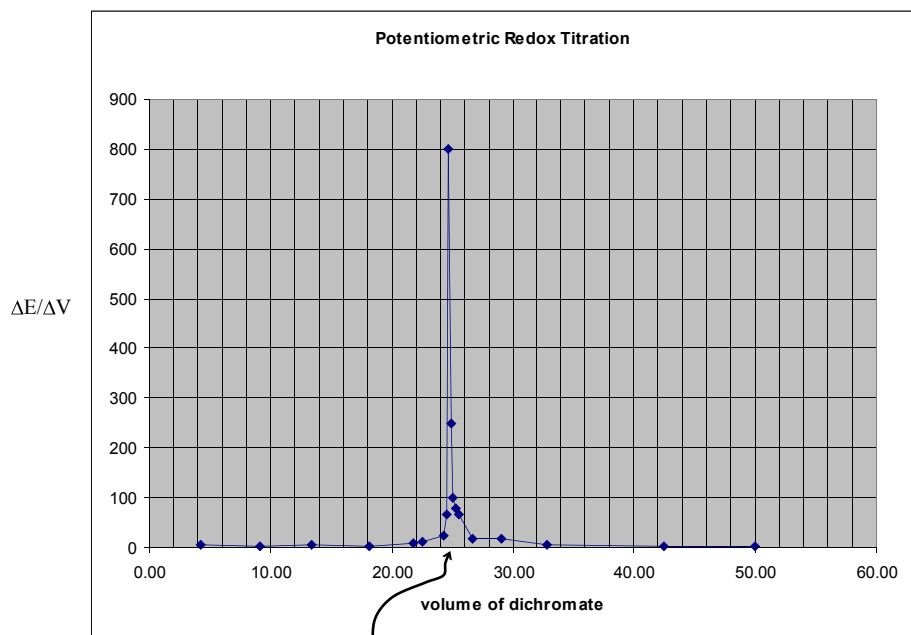
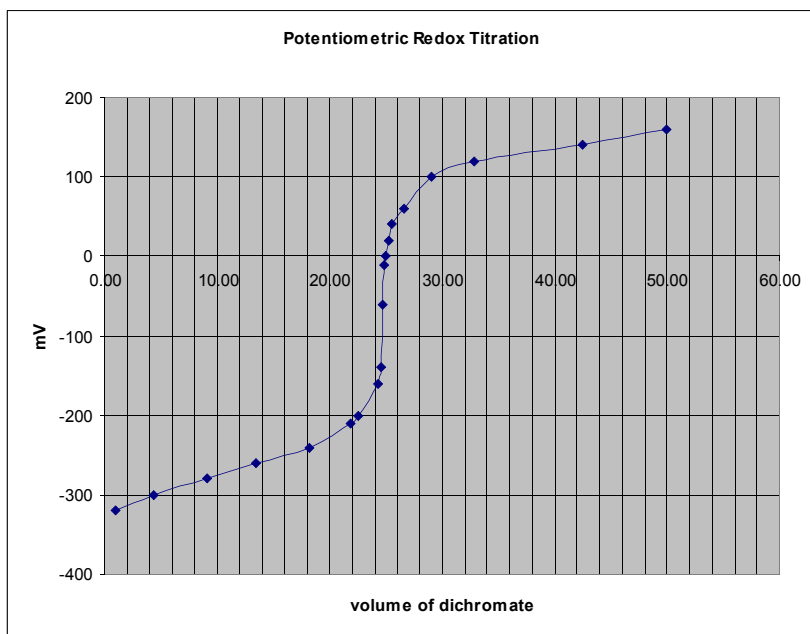
A solution of ammonium iron(II) sulphate was provided which was 0.10 M with respect to iron(II).

Results:

mV	Vol cm^3
-320	1.00
-300	4.30
-280	9.15
-260	13.40
-240	18.20
-210	21.85
-200	22.60
-160	24.30
-140	24.60
-60	24.70
-10	24.90
0	25.00
20	25.25
40	25.55
60	26.65
100	29.00
120	32.80
140	42.50
160	50.00

ΔE	ΔV	$\Delta E/\Delta V$
20	3.3	6.06
20	4.85	4.12
20	4.25	4.7
20	4.8	4.17
30	3.65	8.22
10	0.75	13.33
40	1.7	23.53
20	0.3	66.67
80	0.1	800
50	0.2	250
10	0.1	100
20	0.25	80
20	0.3	67
20	1.1	18.18
40	2.35	17
20	3.8	5.26
20	9.2	2.17
20	7.5	2.67

continued:



From these plots the end point is at 24.70 cm³.

Moles of dichromate used = $24.70 \times 10^{-3} \times 0.017 = 4.2 \times 10^{-4}$ mol

Moles of iron(II) reacted = $6 \times 4.2 \times 10^{-4}$ mol.

This is contained in 25 cm³ of iron(II) solution.

Therefore, concentration of the iron(II) solution = $40 \times 6 \times 4.2 \times 10^{-4} = 0.101$ M.

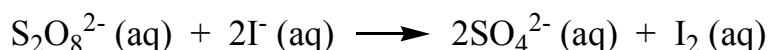
The phosphoric acid lowers the iron(II)/iron(III) redox potential by complexing with iron(III) and provides a larger mV change at the end point.

Experiment XIII

Kinetics:

Investigating the Peroxodisulphate - Iodide reaction

Peroxodisulphate and iodide react according to the following ionic equation:



The reaction is bimolecular and follows a second order rate equation.

$$\text{rate} = k_1 [\text{S}_2\text{O}_8^{2-}][\text{I}^-]$$

However, if the reaction is carried out so that the iodide concentration remains constant then the reaction is first order with respect to peroxodisulphate.

$$\text{rate} = k_2 [\text{S}_2\text{O}_8^{2-}]$$

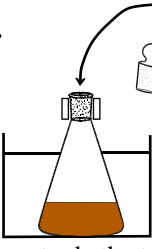
$$\text{where } k_2 = k_1 [\text{I}^-]$$

If the initial concentration of peroxodisulphate is a moles per dm^3 and x moles per dm^3 is the amount used up at time t the rate equation can be expressed as follows:

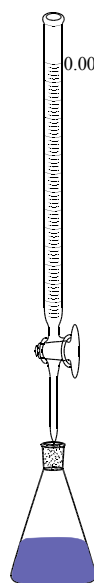
$$t = \frac{1}{k} \ln a - \frac{1}{k} \ln (a-x)$$

Where $(a-x)$ = the concentration of peroxodisulphate at time t .

Procedure:

1.  Add 50.0 cm^3 of 0.04M potassium peroxodisulphate (potassium persulphate) solution.
- Then add 50.0 cm^3 of 0.4M potassium iodide solution. Start the stopclock immediately. Fit stopper and shake the flask to mix thoroughly.
- water bath at 20°C

2.



Titrate 10.0 cm^3 samples of the reaction mixture with standard sodium thiosulphate solution.

This is achieved by withdrawing a 10.0 cm^3 aliquot of the mixture at regular intervals over a 40 minute (2400 sec) period, ie, at 300, 600, 900, 1200, 1500, 1800, 2100 & 2400 seconds after the start.

Each 10 cm^3 aliquot is immediately added to 100 cm^3 of cold distilled water, in a clean 250 cm^3 conical flask, to quench the reaction and then titrated against standard 0.01 M sodium thiosulphate solution using starch indicator.

3. After about an hour and a half take a final reading. By this time the reaction should have finished; this final titre value is known as the *infinity titre* and is denoted V_{∞} .

If titre at time $t = V_t$ and titre at time $\infty = V_{\infty}$

then, $a \propto V_{\infty}$ and $(a-x) \propto (V_{\infty} - V_t)$

hence, $t = 1/k \cdot \ln V_{\infty} - 1/k \cdot \ln(V_{\infty} - V_t)$

A plot of t versus $\ln(V_{\infty} - V_t)$ should give a straight line confirming the first order relationship with respect to peroxodisulphate. The slope of the line = $-1/k$, hence k .

Calculate the value of k at 20°C .

Experiment XIII

Kinetics:

Investigating the Peroxodisulphate - Iodide reaction

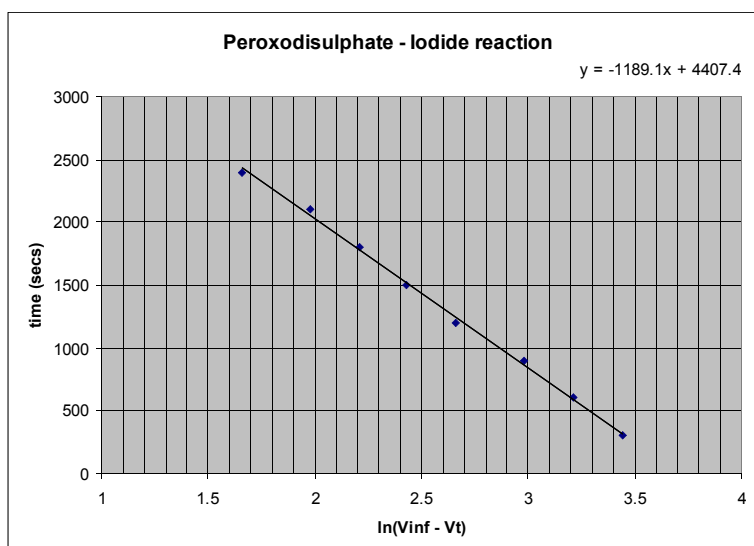
Example of Outcomes

Results:

Time (t, secs)	Titre (V_t , cm^3)
300	8.30
600	14.70
900	19.80
1200	25.20
1500	28.15
1800	30.40
2100	32.25
2400	34.25
∞	39.50

$\ln(V_\infty - V_t)$
3.44
3.21
2.98
2.66
2.43
2.21
1.98
1.66

This straight line relationship confirms first order kinetics with respect to peroxodisulphate.

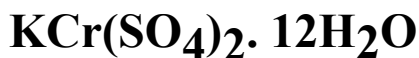


$$-1/k = -1189$$

$$\text{rate} = k = 8.4 \times 10^{-4} \text{ s}^{-1}$$

Experiment XIV

Preparation of Chrome Alum

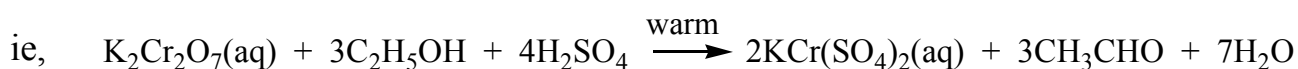


Chrome alum (chromium(III) potassium sulphate dodecahydrate) is a purple coloured crystalline solid. It forms octahedral crystals.

At one time it was used to tan leather and to make photographic film. It is used as a mordant. It is an example of a *double salt* (ie, an ionic compound consisting of two different metal cations in a lattice of anions and water molecules). When dissolved in water it gives a solution containing hydrated potassium ions, chromium(III) ions and sulphate ions.

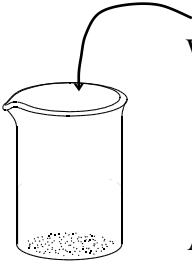
Chrome alum is just one of a large group of compounds having the general formula, $\text{M(I)M(III)}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$. Where M(I) may be, Li, Na, K, Rb, Cs, Ag, Tl or NH_4 and M(III) may be, Al, Cr, Fe, Mn, Co, Ga, etc. These compounds are collectively known as *alums*, from the Latin, *alumen* (aluminium also derives its name from this Latin word!).

In this exercise chrome alum is prepared by reducing potassium dichromate with ethanol.



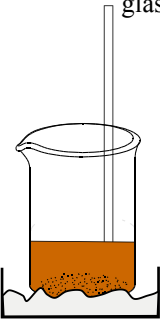
Some ethanal will be oxidised to ethanoic acid. Crystallising the final reaction mixture gives chrome alum.

Procedure: Wear protective spectacles. Use the apparatus under a fume hood.

- 

300 cm³ beaker

Weigh out 10.0 g of potassium dichromate crystals and introduce into a beaker.

Add 75 cm³ of distilled water (at about 60°C) and stir to dissolve.
- 

glass rod

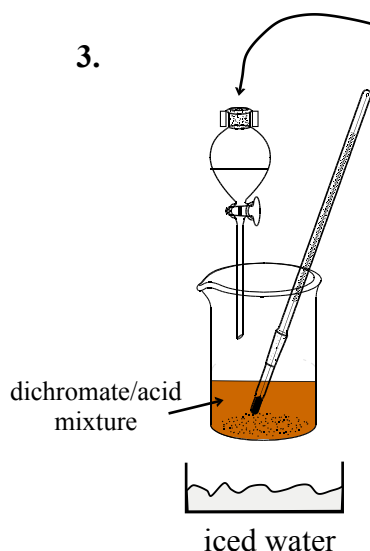
cold water

Cool to near room temperature and add 10 cm³ of concentrated sulphuric acid carefully, a little at a time, with stirring (**CARE: concentrated H₂SO₄ is highly corrosive**).

After adding the acid, cool the mixture again.

continued:

3.



Introduce 15 cm³ of IMS (95% ethanol) into a small dropping funnel and add **slowly** and **carefully** to the stirred dichromate/acid mixture.

Stir **carefully** with the thermometer and ensure that the reaction temperature does not rise above 60°C.

As necessary, use iced-water to cool the beaker containing the reaction mixture.

This temperature requirement is important because at higher temperatures the formation of complex ions (rather than the simple ions) occurs and the resulting mixture is difficult to crystallise.

A colour change occurs as orange dichromate is reduced to greenish blue chromium(III).

Toxic ethanal fumes may issue from the reaction mixture.

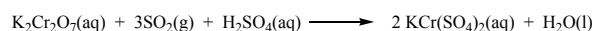
Note:

Reducing agents other than ethanol can be used.

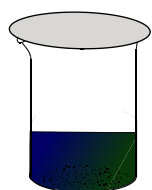
eg,

If a small cylinder of **sulphur dioxide** is available, the gas can be bubbled through the dichromate/acid until there is no further colour change.

This would, of course, be performed in a fume cupboard since the gas is toxic.



4.



greenish-blue solution

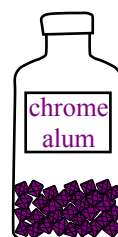
Cover the beaker and set aside for some days until crystallisation is complete.

Filter the contents of the beaker and wash the crystals with a little distilled water (do not use too much since the crystals are soluble in water).

Spread the crystals out on filter paper and allow to air dry.

Weigh the crystals and store in a labelled container.

5.



purple coloured chrome alum crystals

6.

Chrome alum is a double salt and when dissolved in water it provides a solution containing hydrated potassium, chromium(III) and sulphate ions.

It should be possible to confirm the presence of these ions by applying suitable qualitative tests on the aqueous solution.

Test for chromium(III) with sodium hydroxide solution, sulphate with barium chloride solution and potassium with the flame test.

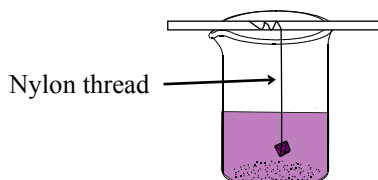
7.

Growing crystals:

Chrome alum is very soluble in water (about 200g per 100g of water). The saturated solution is darkly coloured and it is difficult to see the crystal growing.

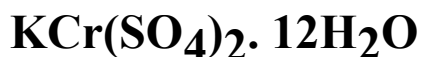
A better alternative is to grow a crystal in a mixture of saturated chrome alum and saturated potash alum (ie, potassium aluminium sulphate). This way the colour of the solution can be adjusted by varying the proportions of chrome alum and potash alum solutions used. The end result will be a crystal of chrome alum embedded in mixed crystal of chrome alum and potash alum!

Potash alum ($\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$) is made by dissolving 7 g (0.04 mol) potassium sulphate in 30 cm³ of distilled water and 20 cm³ of 1M sulphuric acid. Stir in 27g (0.04 mol) of hydrated aluminium sulphate ($\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$). Heat the mixture to dissolve the salts. Filter and leave the filtrate to crystallise in a suitably sized, covered, evaporating basin. Filter off the crystals and air dry.



Experiment XIV

Preparation of Chrome Alum



Example of Outcomes

Moles of potassium dichromate used: $10.0/294 = 0.034 \text{ mol}$

Moles of alum expected = $0.034 \times 2 = 0.068 \text{ mol}$

Mass of alum expected = $0.068 \times 499 = 34 \text{ g}$

Mass of chrome alum crystals obtained = 23.0 g

% yield = $(23/34) \times 100 = 68\%$

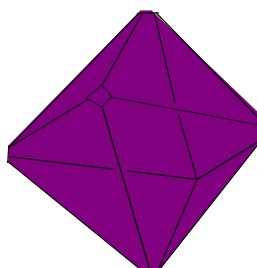
Melting point = 89°C

A solution of the alum gave a light green precipitate of hydrated chromium(III) hydroxide with dilute sodium hydroxide solution. This dissolved in excess hydroxide to give a green solution containing chromite ions ($[\text{Cr}(\text{OH})_4(\text{H}_2\text{O})_2]^-$). This indicates the presence of chromium(III) ions.

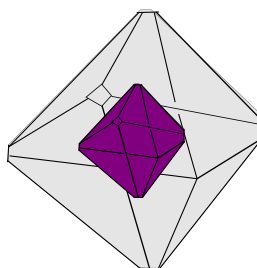
A solution of the alum gave a whitish precipitate of barium sulphate when treated with dilute barium chloride and dilute hydrochloric acid. This indicates the presence of sulphate ion.

A flame test on a solution of the alum gave a lilac colouration indicating potassium.

chrome alum crystal



chrome alum crystal
in potash alum crystal



Experiment XV

Mini Project

(Organic Based)

Performing synthetic organic chemistry has its ups and downs! Sometimes a synthesis goes exactly according to plan and gives a good yield of the expected product. On other occasions the synthesis may be a total failure with little or no yield of the required product. Sometimes a reaction occurs and provides a good yield of product but, on examination, it is not the required product! However, these failures and disappointments can sometimes be turned to advantage. A classic and often quoted example concerns Sir William Henry Perkin's attempt to make quinine (used to treat malaria). He thought that by reacting aniline (benzenamine) with potassium dichromate some quinine would be formed. Unfortunately the result was a tarry mess! However, being very observant, he noticed that his reaction mixture had a purplish hue so he added alcohol hoping to extract the coloured material. Evaporating the alcohol extract left a purple coloured solid. It transpired that this solid was an excellent dye for silk and in 1858 the Perkin's family started manufacture of the dye which they called Aniline Purple (also known as Mauveine).

Although present day organic chemists have a wealth of knowledge and understanding, developed since Perkin's time, their syntheses can still throw up the unexpected. When this happens explanations must be found.

The procedure described below provides a simple example of a reaction which would be difficult to predict without a knowledge of modern reaction mechanisms.

Follow the preparative procedure and analyse the product. Having established the identity of the product suggest a reaction mechanism.

Procedure:

**CARE: Concentrated sulphuric acid is highly corrosive.
Avoid skin contact. Wear safety spectacles.**

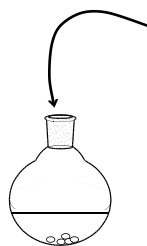
1.



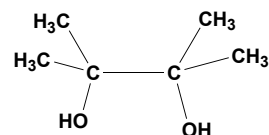
Add 60 cm³ of 4.5 M sulphuric acid.

Note: Could make up the acid, in the flask, by adding 14 cm³ of concentrated sulphuric acid, *slowly and very carefully with swirling*, to 45 cm³ of distilled water

2.

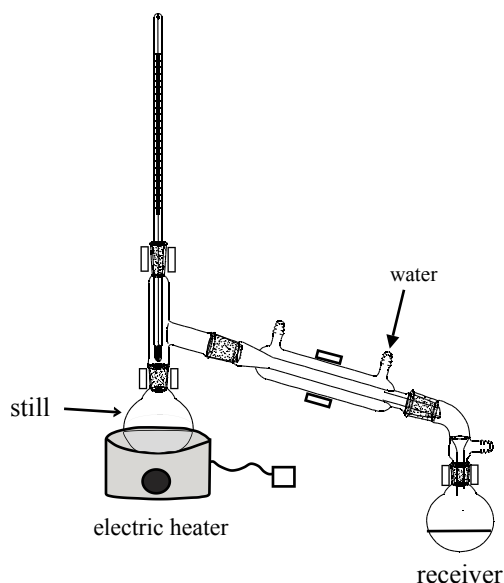


Add a few antistatic granules and from a beaker *gradually* add 10g (0.044 mol) of 2,3-dimethylbutan-2,3-diol hexahydrate (or 5.5 g, 0.046 mol, of anhydrous 2,3-dimethylbutan-2,3-diol) to the acid in the flask. Swirl the flask to mix the reactants.



continued:-

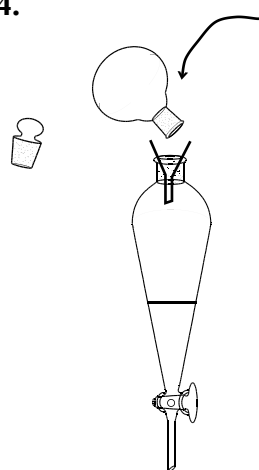
3.



Fit the reaction flask with a still head, thermometer (0 - 250°C), condenser, etc, as for simple distillation. Using an electric heating mantle **slowly** raise the temperature of the reaction mixture. Provide time for the reaction to take place (say 10 to 15 mins) before allowing distillation to proceed. Distil, **slowly**, discarding any distillate coming over below 100°C. As the distillation proceeds, two phases should collect in the receiver, a lower aqueous phase and an upper organic phase (they should be about equal in volume). The distillation is complete when the upper layer (ie, the layer containing the required organic product) no longer increases.

Turn off and remove the heat source and **allow the apparatus to cool**. Carefully remove the *receiver* and the *still*. Stand the *receiver* on a cork ring. Transfer the *still* to a fume cupboard (if it is not already in one!) and carefully pour its contents (**Care: acid!**) into a large volume of water in a beaker. Discard the contents of the beaker down the fume cupboard sink, washing away with water.

4.



Pour the contents of the receiver into a separating funnel. Mix with 40 cm³ of ether (**CARE: Highly volatile and flammable**). Allow the layers to separate. Run off and discard the lower aqueous layer (washing away down the fume cupboard sink). To the remaining ether layer, carefully add 50 cm³ of 10% sodium carbonate solution. Swirl the funnel to mix the contents (CO₂ is evolved). Stopper the funnel and invert to mix (**CARE: allow for expansion. With the funnel inverted turn the tap to allow gas to escape. Check with your supervisor if you are not familiar with this technique!**). Allow the layers to separate and discard the lower aqueous layer as previously. Wash the ether layer with 15 cm³ of distilled water. Discard the lower aqueous layer. The remaining ether layer contains the required organic product.

5.

Run the ether extract into a clean, dry, beaker. Add a couple of spatulas of anhydrous sodium sulphate. Stir and leave to stand a few minutes. Decant off the dry ether extract into another clean beaker. Rinse the drying agent with 10 cm³ of fresh ether and combine the ether solutions.

Evaporate the ether by warming the solution on an electrically heated water bath in a fume cupboard.*

Pipette the remaining organic product into a weighed sample bottle. Determine the mass & boiling point of product.

* **Note:** At this stage, having removed the majority of the ether, by evaporation, the ideal is to distil off the remaining ether in a **small** scale distillation apparatus (**taking the usual precautions when heating flammable ether solutions**) and then continue distilling collecting the main organic fraction and noting its mean boiling range. This gives a purer product for further analysis.

6.

Characterise the organic product.

- (i) Test for unsaturation with dilute permanganate solution &/or bromine water.
- (ii) Test for the carbonyl group by adding to Brady's reagent (ie, 2,4-dinitrophenylhydrazine reagent).
- (iii) Test for the carbonyl group with semicarbazone hydrochloride.
- (iv) Test with Tollen's reagent.
- (v) Prepare solid derivative(s) and measure melting point(s).
- (v) Obtain the infra-red spectrum (as a thin film). Identify significant structural features.

The mass spectrum shows peaks at 15, 29, 41, 43, 57 (base peak), 85 and 100 (M⁺).

Identify the major reaction product and write a possible reaction mechanism.

continued:

Experiment XV

Mini Project

(Organic Based)

Example of Outcomes

1.
Relative molecular mass of reaction product = 100 (provided by mass spectrum)
Maximum yield = 0.045 mol = 4.5 g (assumes 1 mol of reactant gives 1 mol of product)
Actual yield = 2.8 g
% yield = 62%

Mean boiling temperature of reaction product = 106°C (from distillation).

Very slight decolourisation of permanganate and bromine water. This indicates the presence of some alkene.
Orange precipitate with 2,4-DNP reagent. This indicates the presence of a carbonyl group (ketone or aldehyde).

White precipitate with semicarbazide HCl. This indicates carbonyl group.

Negative silver mirror test with Tollen's reagent. Aldehyde group absent.

Thin film infra-red spectrum shows large, sharp, peaks at 2900-2800, 1695, 1350, 1140 cm⁻¹ indicating, CH₃ (CH stretching), C=O (stretching), t-butyl (sym bending), t-butyl (skeletal). Little or no absorption just above 3000 cm⁻¹ (no unsaturated CH str).

The mass spectrum gives molecular mass as 100 and indicates the presence of aliphatic hydrocarbon groups (since there are a large number of peaks at odd mass numbers (eg, base peak at m/e 57 corresponding to (C₄H₉)⁺ - which could be t-butyl)

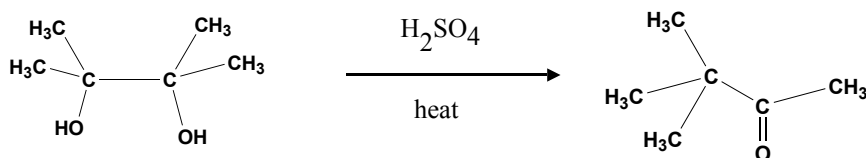
2,4-DNP and semicarbazone derivatives were prepared and recrystallised from ethanol.

2,4-DNP melting point = 124°C.

Semicarbazone melting point = 156°C.

These results correspond most closely with 3,3-dimethylbutanone as the major reaction product.

ie,

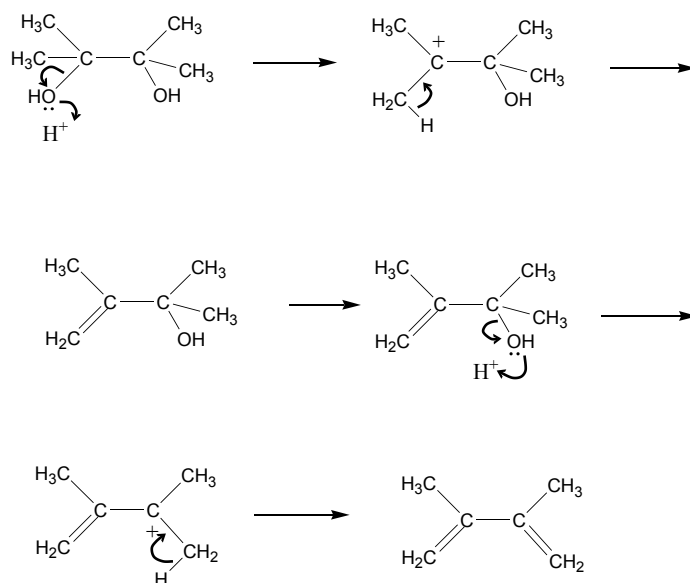


continued:

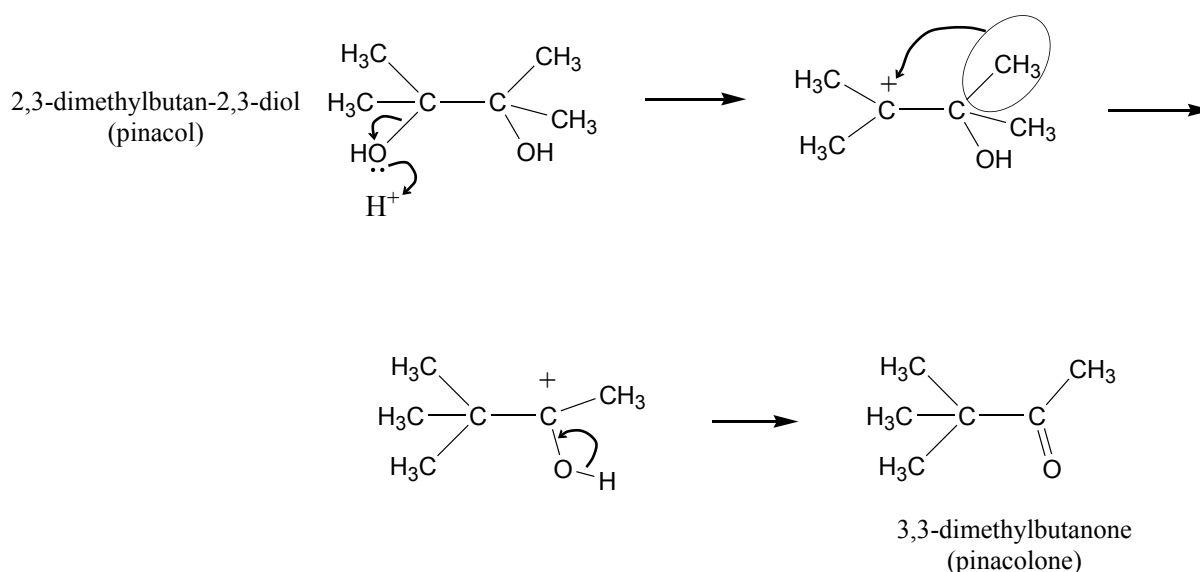
Reactions mechanisms:

A-level students will be aware that alcohols can be dehydrated to give alkenes by reaction with concentrated sulphuric acid. When ethanol, for example, is heated with concentrated sulphuric acid ethene is produced. On this basis it would be reasonable to expect 2,3-dimethylbutan-2,3-diol to provide 2,3-dimethylbuta-1,3-diene when heated with concentrated sulphuric acid. In this preparation we are using 4 to 5 molar sulphuric rather than the concentrated even so one would expect some of the diene to be formed.

The diene boils at 69°C so in this preparation most of it would be discarded in the early stages of the distillation (ie, *discard fractions boiling below 100°C*).



Less predictable is the formation of a ketone. However, this is a distinct possibility since when water is lost, in the first stage, a relatively stable tertiary carbocation ion formed. This then converts into an even more stable carbocation resulting from a 1,2-shift of a methyl group. This is an example from a group of reactions, involving changes in carbon skeleton, known as Wagner-Meerwein rearrangements.



This reaction is known as the pinacol-pinacolone rearrangement.

Experiment XVI

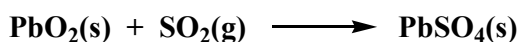
Preparation & Analysis of a Group IV Oxide.

Lead(IV) Oxide.

The group IV oxides range from acidic carbon dioxide to the amphoteric oxides of tin and lead.

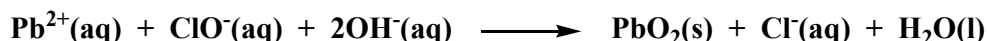
The blackish-brown lead(IV) oxide reacts with concentrated hydrochloric acid forming the tetrachloride which then reacts with excess acid giving hexachloroplumbate(IV), PbCl_6^{2-} . It also reacts with concentrated sodium hydroxide forming hexahydroxoplumbate(IV), $\text{Pb}(\text{OH})_6^{2-}$.

Lead(IV) oxide is a powerful oxidising agent, oxidising sulphur dioxide to sulphate and warm, concentrated, hydrochloric acid to chlorine:

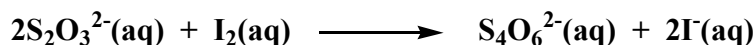
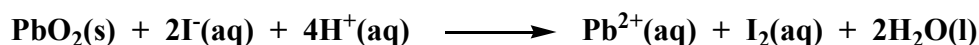


Its principal applications include, the coating on the positive electrode in the lead accumulator, oxidant in matches and a component of high voltage lightning arresters (these protect electrical insulators against power surges from lightning strikes).

Lead(IV) oxide can be made by dissolving lead in nitric acid, and then adding sodium hydroxide solution followed by sodium chlorate(I) solution and heating the mixture.



Following isolation of the oxide its purity can be estimated by using it to oxidise iodide to iodine and estimating the iodine liberated by titration against standard thiosulphate solution.



Procedure: **Wear protective spectacles. Use a fume cupboard and protective gloves as necessary.**

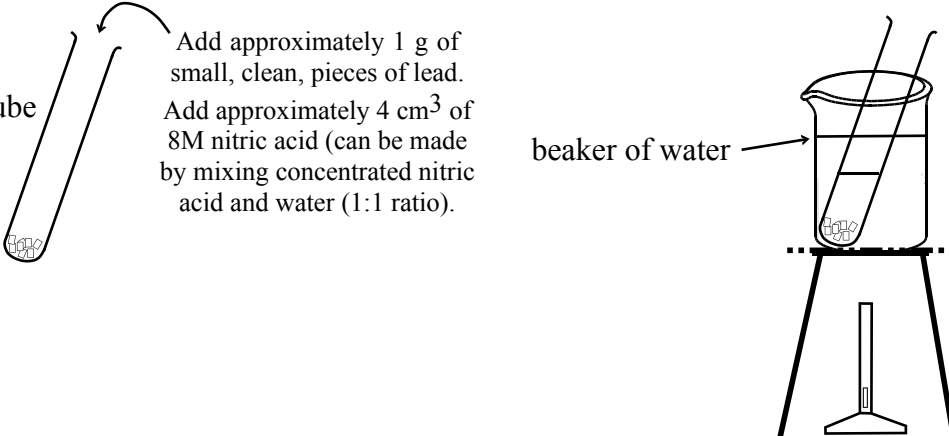
1.

boiling tube

Add approximately 1 g of small, clean, pieces of lead.
Add approximately 4 cm³ of 8M nitric acid (can be made by mixing concentrated nitric acid and water (1:1 ratio).

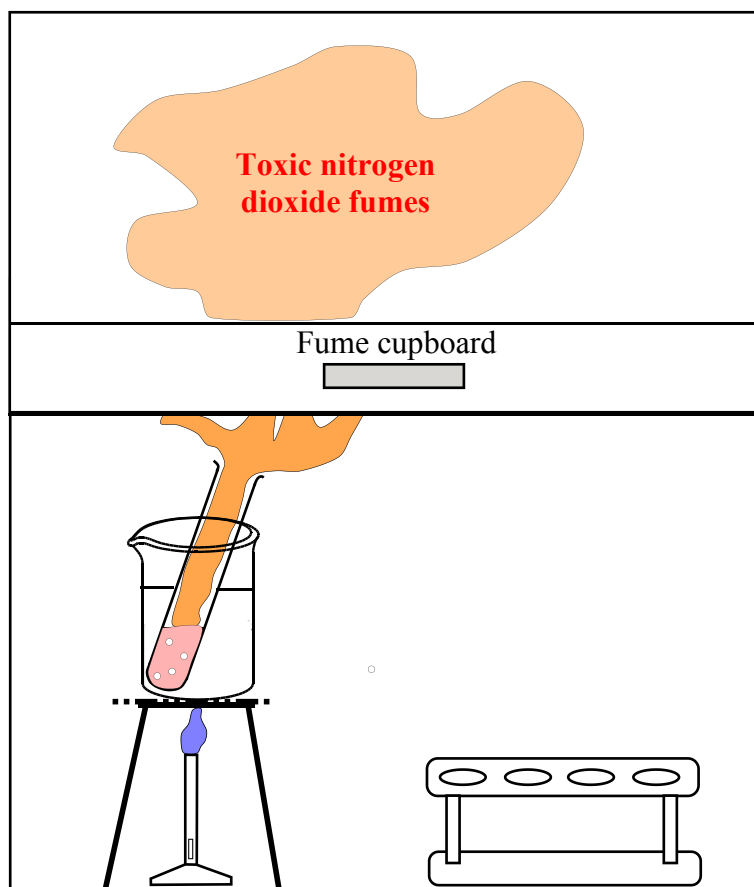
beaker of water

Place the tube in a beaker of water set up in a fume cupboard.



continued:

3.



Heat the water in the beaker to speed up the reaction of the metal with nitric acid.

Using a test tube holder remove the tube occasionally from the hot water to control the speed of reaction.

When all of the lead has dissolved, remove the tube from the beaker and allow it to cool in a test-tube rack.

4.

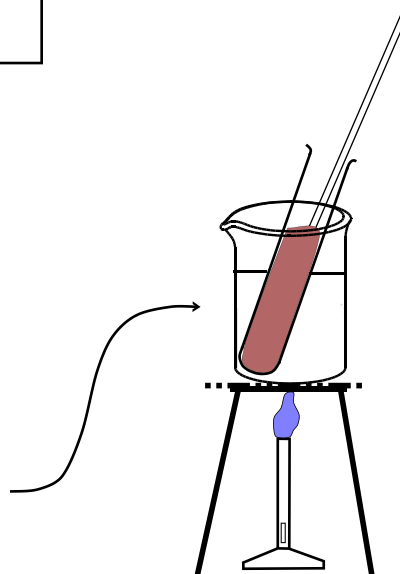
When cool add 2M sodium hydroxide solution gradually, from a test pipette, until a faint white precipitate of lead hydroxide just appears. At this stage the majority of the lead is present in solution as lead(II) nitrate.

Next add 10 cm³ of 2M sodium hydroxide and 6 cm³ of 2M sodium chlorate(I) (CARE: this is bleach, ie, 15% sodium hypochlorite solution).

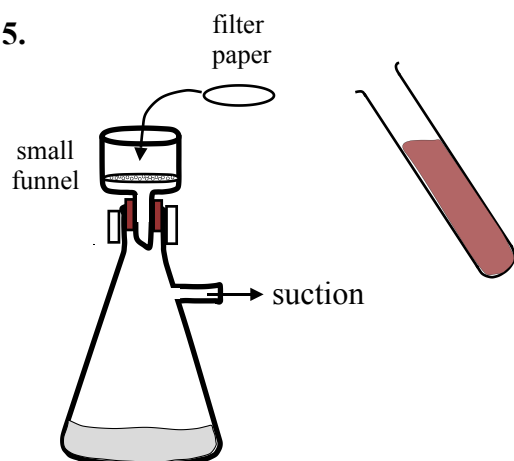
Stir the mixture which should be white.

With stirring, heat the tube in a beaker of hot water.

The contents of the tube will turn brown as the lead(IV) oxide is formed.



5.



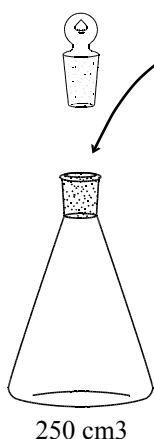
Filter off the lead oxide. Wash with water. Dry and weigh. Introduce into a labelled sample vial. Calculate the % yield based on 1g of lead (ie, 0.0048 mol)



continued:

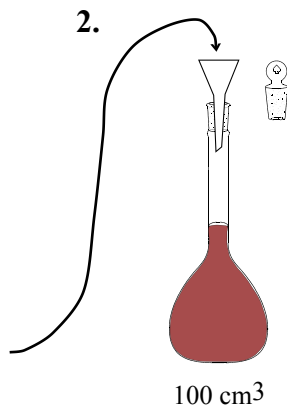
Estimating the Purity of Lead(IV) oxide.

1.

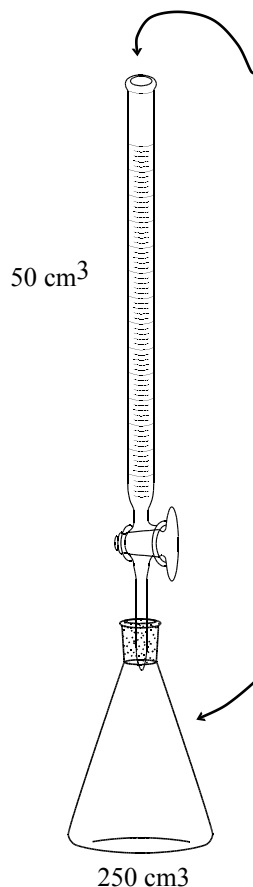


Weigh accurately a quantity of lead(IV) oxide (eg, 0.30 g) into a conical flask.
Add approximately 1 g of potassium iodide and 50 cm³ of 2M hydrochloric acid.
Stopper the flask and mix the contents. Continue swirling the contents, at intervals, for about 10 minutes until no more iodine is produced.
Wash the reaction mixture into a graduated volumetric flask. Make up to the mark with distilled water.

2.

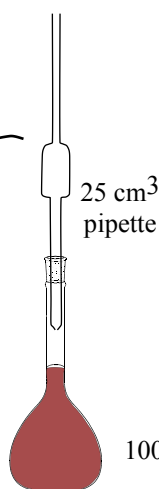


3.



Fill the burette with 0.03M sodium thiosulphate solution.

Introduce 25.00 cm³ of the reaction mixture (ie, iodine solution) into the titration flask and titrate against the thiosulphate solution using starch indicator.
Repeat the titration and take a mean value.



100 cm³ of iodine solution

4.

Use your results to calculate the amount of lead dioxide (ie, grams or moles) reacting with the iodide.
Compare this with the amount of lead dioxide weighed out and calculate the % purity of your sample of lead dioxide.

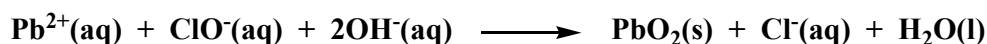
continued:

Experiment XVI

Preparation & Analysis of a Group IV Oxide.

Lead(IV) Oxide.

Example of Outcomes



From equations:

3 mol of lead gives 3 mol lead nitrate

1 mol lead nitrate gives 1 mol of lead dioxide.

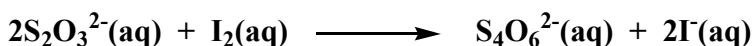
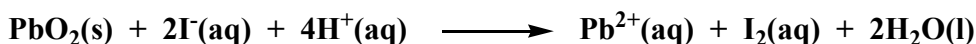
3 mol of lead gives 3 mol of lead dioxide.

Mol of lead used = $1/207 = 0.00483$

Mol of lead dioxide = 0.00483 (max)

Mass of lead dioxide obtained = 0.51 g (ie, 0.00213 mol)

% yield = $(0.00213/0.00483) \times 100 = 44\%$ (low yield, possible incomplete reaction and/or material lost in work up)



From equations:

1 mol of lead dioxide gives 1 mol of iodine.

1 mol of iodine reacts with 2 mol of thiosulphate.

1 mol of lead dioxide is equivalent to 2 mol of thiosulphate.

Mass of lead dioxide used 0.30 g.

First titre value = 20.10 cm³

Second titre value - 20.20 cm³

Mean titre = 20.15 cm³

Mol of thiosulphate used per titre = $(20.15/1000) \times 0.03 = 0.000605$

Equivalent amount of lead dioxide = $0.5 \times 0.000605 = 0.000303$

Scale up: $4 \times 0.000303 = 0.00121$ mol lead dioxide.

Mass of lead dioxide = 0.289 g

% purity = $(0.289/0.30) \times 100 = 96.3\%$

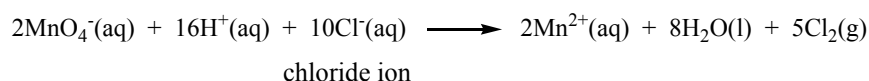
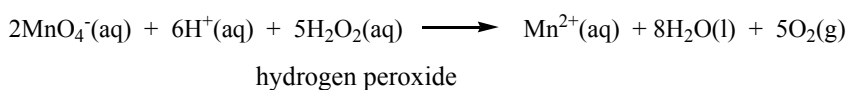
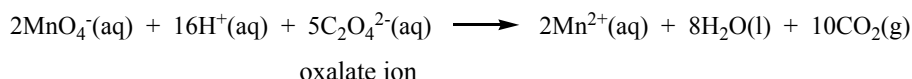
Experiment XVII

Kinetics

Investigating the reaction between Permanganate & Oxalate

Potassium permanganate is a deep purple coloured crystalline solid. It is a powerful oxidising agent:

eg,

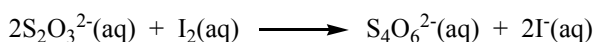
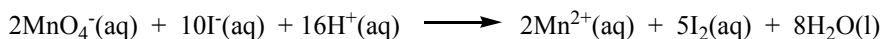


Its reaction with oxalate at room temperature is fairly slow initially but quickens as the reaction proceeds. Manganese(II) ions, formed as the reaction occurs, are considered to act catalytically. The manganese(II) is acting as a, so called, *autocatalyst* (a reaction product which speeds up the reaction). The reaction also provides an example of *homogeneous catalysis*.

It is worth noting that a variable quantity of manganese dioxide is also formed in this reaction and some researchers consider that the dioxide *also* behaves as an autocatalyst (however, its action would be an example of *heterogeneous catalysis* because it is formed as a finely divided solid!).

In the experiment which follows, *two* reaction mixtures (A & B) are examined. In the second of these mixtures the reactant concentrations are halved and in both mixtures the oxalate is in excess (so its concentration throughout the reaction remains about constant). On the other hand, the concentration of the permanganate decreases significantly during the course of the reaction.

The concentration of the permanganate is determined, at intervals (time, t), by adding a portion of the reaction mixture to potassium iodide solution when iodine is liberated. This is estimated by titration against standard sodium thiosulphate solution using starch indicator. The concentrations of permanganate, at times t, are proportional to the thiosulphate titre values.



In order to ensure a uniform change in the rate of reaction both reaction mixtures contain a quantity of the catalytic manganese(II) ions.

Theory shows that in a case like this,

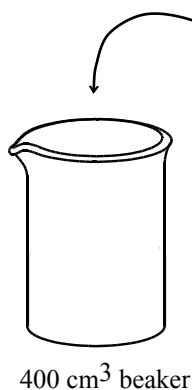
$$\frac{t_{0.5}^A}{t_{0.5}^B} = \left[\frac{a_B}{a_A} \right]^{n-1}$$

$t_{0.5}$ = half life, a = initial concentration in stated mixture, n = order

continued:

Procedure:

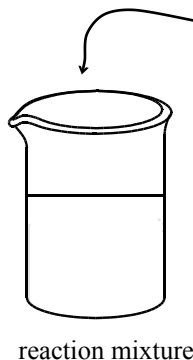
1.



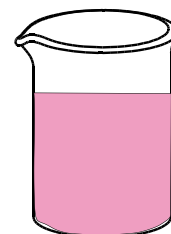
Introduce into the beaker:

200 cm³ 0.10M sodium oxalate,
10.0 cm³ 1M sulphuric acid,
25 cm³ 0.2M manganese(II) sulphate,
15 cm³ distilled water.

2.

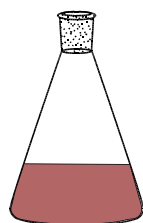


Add 50.0 cm³ 0.02M potassium permanganate.



(total volume = 300 cm³)

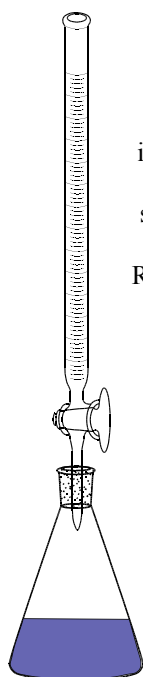
3.



Start a stop clock.

As soon as possible, pipette out 25 cm³ of the reaction mixture into 20.0 cm³ of 0.30M potassium iodide in a 250 cm³ conical flask. **Note the time (t).**

4.



Titrate the liberated iodine against 0.01M sodium thiosulphate solution using starch indicator. Record the titre value.

5.

At 5 minute intervals (note the times over about half an hour) pipette out further 25 cm³ aliquots of the reaction mixture & on each occasion add to 20 cm³ of 0.30M KI solution. Titrate each one against the thiosulphate solution recording the titre values.

Tabulate your results for reaction mixture A

6.

Repeat the whole exercise using a reaction mixture (B) which has *half* the concentration of permanganate ion as in mixture A.
eg,

200 cm³ 0.1M sodium oxalate,
50 cm³ 0.02M potassium permanganate,
10 cm³ 1M sulphuric acid,
25 cm³ 0.2M manganese(II) sulphate,
315 cm³ distilled water.

Total volume of mixture = 600 cm³.

Tabulate your results.

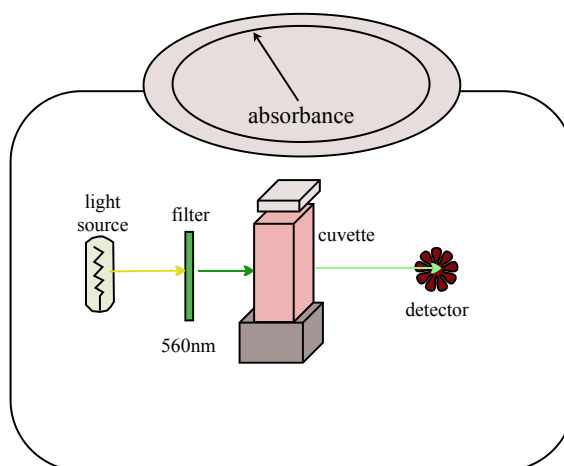
Plot two graphs, one for mixture A and one for mixture B, of *time* (secs) versus *titre of sodium thiosulphate*. In each case determine the half life ($t_{0.5}$).

Calculate the order of the reaction with respect to permanganate using the relationship given in the introduction.

continued:

As an alternative to the titrimetric exercise, the permanganate-oxalate reaction can be studied colorimetrically.

colorimeter



Procedure:

Calibration curve.

Prepare the following permanganate solutions.

solution	0.02M perman-ganate (cm ³)	water (cm ³)	molarity
1	1	50	4×10^{-4}
2	0.5	50	2×10^{-4}
3	0.5	100	1×10^{-4}
4	0.5	125	0.8×10^{-4}
5	0.5	150	0.66×10^{-4}

Place a cuvette containing distilled water into a colorimeter and using a suitable filter (eg, green) adjust to read 100% transmission.

Place each permanganate solution (ie, 1 - 5) into the colorimeter and read off the corresponding absorbance.

Plot a graph of absorbance against concentration (the *calibration curve*).

The Investigation.

Introduce 2.0 cm³ of 0.002M potassium permanganate solution into a test tube. Fit the tube with a rubber stopper.

Zero a stop clock ready for use.

Using a small measuring cylinder add, to the test tube, 8.0 cm³ of a solution which is 0.125M with respect to oxalic acid and 1.5M with respect to sulphuric acid (**CARE: poisonous and corrosive, keep away from skin**).** Stopper the tube, mix the contents by inverting the tube, and **start the stop clock**. Using a teat pipette add some of the mixture to a cuvette and measure the absorbance of the mixture every 20 seconds for about 5 minutes. Referring to the calibration curve obtained earlier convert absorbance values to concentration values and then plot a graph of concentration against time.

Repeat the experiment but this time add 6 drops of 0.02M manganese sulphate solution to the oxalate solution before mixing with the permanganate solution. Again, plot a graph of concentration against time and compare with the first graph.

**100 cm³ of this mixture can be made by adding 25 cm³ of distilled water to 75 cm³ of 2M sulphuric acid and then dissolving into this 1.125g of oxalic acid.

Experiment XVII

Kinetics

Investigating the reaction between Permanganate & Oxalate

Example of Outcomes

Background theory:

For a reaction of the nth order,

$$dx/dt = k(a-x)^n$$

where a = initial concentration and x = concentration used up at time t.

integration of this between 0, t and 0,x gives,

$$kt = \frac{1}{(n-1)} \left\{ \frac{1}{(a-x)^{n-1}} - \frac{1}{a^{n-1}} \right\}$$

For initial concentrations a_A and a_B the corresponding half lives, $t_{0.5}^A$ & $t_{0.5}^B$ are given by,

$$t_{0.5}^A = \frac{1}{(n-1)k} \left(\frac{2^{n-1} - 1}{a_A^{n-1}} \right)$$

$$t_{0.5}^B = \frac{1}{(n-1)k} \left(\frac{2^{n-1} - 1}{a_B^{n-1}} \right)$$

From which,

$$\frac{t_{0.5}^A}{t_{0.5}^B} = \left(\frac{a_B}{a_A} \right)^{n-1}$$

If $a_B = 0.5 a_A$ this becomes,

$$\frac{t_{0.5}^A}{t_{0.5}^B} = (0.5)^{n-1}$$

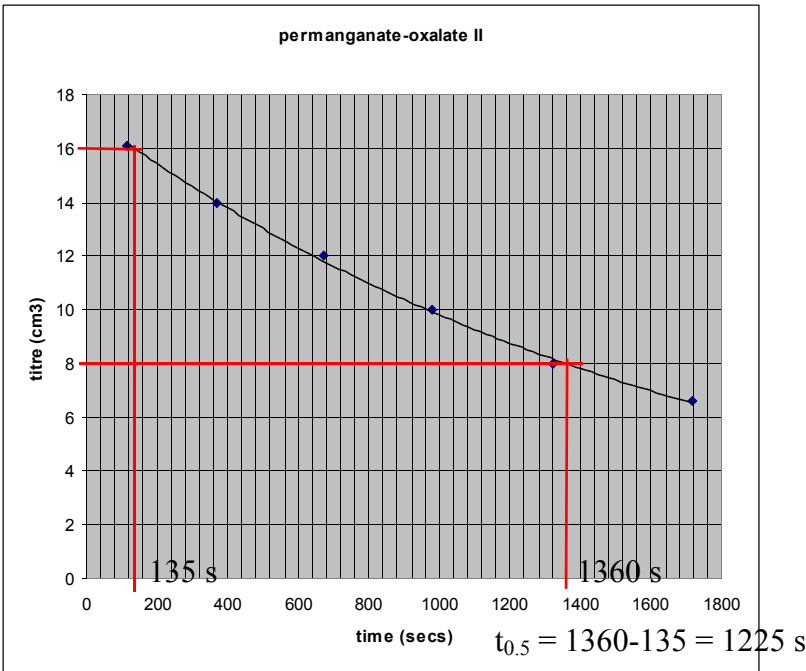
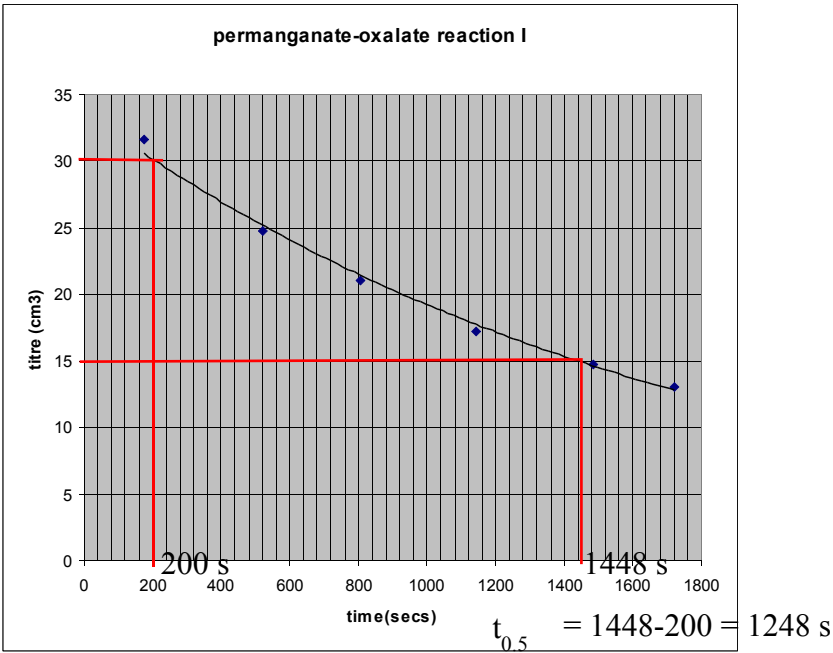
By determining the half lives for the two different initial concentrations the reaction order can be calculated.

ccontinued:

Results:

Mixture I	
Time(s)	Titre (cm3)
174	31.6
522	24.8
805	21.05
1145	17.2
1485	14.75
1722	13.1

Mixture II	
Time (s)	Titre (cm3)
115	16.1
367	14.0
670	12.0
980	10.0
1320	8.0
1715	6.6



Therefore,

Since,
$$\frac{t_{0.5}^A}{t_{0.5}^B} = (0.5)^{n-1}$$

$$1248/1225 = (0.5)^{n-1}$$

$$\log(1.0188) = n-1 (\log(0.5))$$
$$= n-1 (-0.301)$$

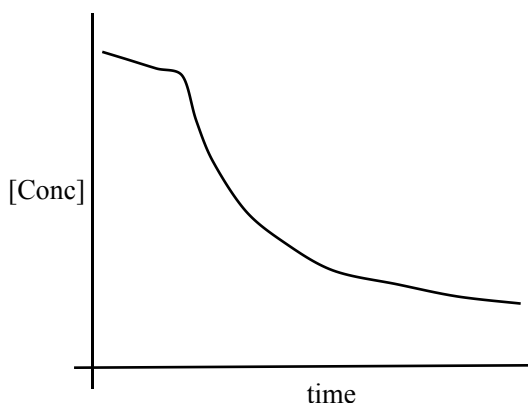
$$n-1 = 0.008089 / -0.301 = -0.02687$$

$$n = 0.97$$

Therefore the order with respect to permanganate is 1 (ie, *first order*)

The Colorimetric Exercise.

The graph of concentration against time begins slowly and then proceeds more rapidly.



The reason for this is that initially, there are little or no catalytic Mn(II) ions and the reaction proceeds slowly. Then, as a few Mn(II) ions are formed, the rate increases and proceeds following first order kinetics with respect to permanganate ions.

Adding Mn(II) ions at the beginning of the reaction results in a smooth decrease in concentration with time from the outset

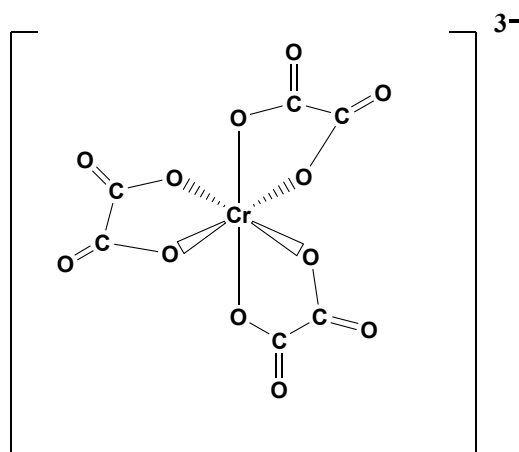
Experiment XVIII

Preparation & Analysis of a Transition Metal Complex

Potassium Trioxalatochromium(III)

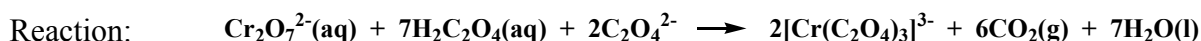
A characteristic property of transition metals is that they form **complex ions**. Complex ions have a central metal ion joined to a number of molecules or ions (usually four or six) each of which has a lone pair of electrons it can donate to the central metal ion to form a bond.

In this preparation a complex ion is formed which has a central chromium(III) ion bonded to three oxalate (ethanedioate) ions arranged octahedrally.

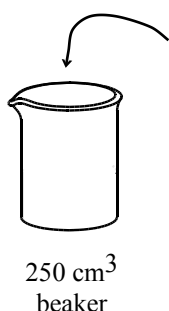


It is isomorphous (ie, same type of chemical formula and crystalline shape) with the trioxalato complexes of Al, Fe and Co. It also exhibits stereoisomerism. This means that it forms different three dimensional structures. The mirror image of the above structure, for example, is non superimposable on the object. The object structure rotates plane polarised light in one direction and the mirror image structure rotates, to the same extent, but in the opposite direction. We say the structures are **chiral** (they have a right and left hand relationship).

Procedure:

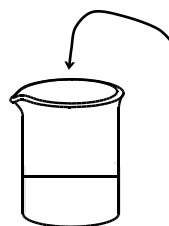


1.



Add 1.9g (0.01 mol) of potassium oxalate monohydrate (**Care: Toxic**). Dissolve in 50 cm³ of distilled water.
Add 4.4g (0.035 mol) of oxalic acid dihydrate (**Care: Toxic**); warm and stir to dissolve.

2.



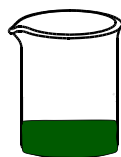
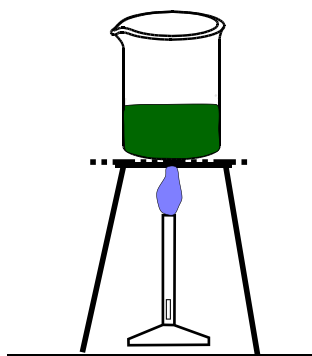
After allowing the mixture to **cool**, add 1.5g (0.005 mol) of potassium dichromate, **a little at a time**, with stirring.

Allow to react until no more carbon dioxide is evolved.

Note: CO₂ is evolved at this stage. Take care to avoid breathing any spray from the beaker.

3.

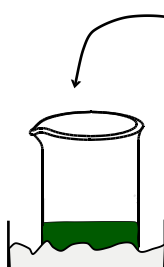
In the fume cupboard, evaporate the mixture to about half volume.



Allow the mixture to **cool** and then stir in about 5 cm³ of IMS.

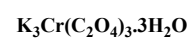
4.

Cool the mixture in iced water.



iced water

When crystallisation is complete, filter and wash the crystals with a little ice cold water and then with IMS. Allow the crystals to dry at room temperature.



487.4



When dry weigh your product.
Calculate % yield.
Store in properly labelled vial.

continued:

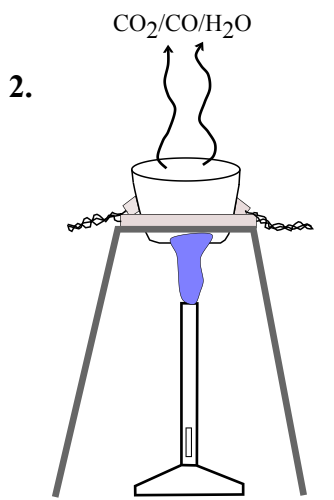
Analysis of Potassium trioxalatochromium(III) crystals

Gravimetric and Colorimetric Analysis.

Gravimetric Analysis:

Procedure:

1. Weigh a crucible to two decimal places.
Add 1.00g of potassium trioxalatochromium(III) trihydrate to the crucible.



Heat the crucible in a fume cupboard or well ventilated area to decompose the chromium complex.

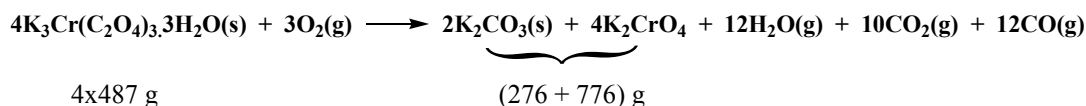
This may take about 35 minutes of gentle, moderate, heating. Check that the decomposition is complete by periodically cooling and weighing the crucible until it has come to constant weight.

A colour change occurs during the decomposition from dark green to yellow.

3. Cool the crucible and record its final mass.

Work out the loss of mass and convert this to a % loss of mass. Compare this with the theoretical, expected, % loss based on the following decomposition equation.

Within experimental error do the experimental and theoretical %'s agree?



Colorimetric Analysis:

The amount of yellow chromate left in the crucible can be estimated by colorimetric analysis.

Procedure:

1.

Make up an alkaline 0.1M potassium chromate solution by adding 4.85g of the chromate to a 250 cm³ graduated volumetric flask and dissolving in about 100 cm³ of distilled water. Add 25 cm³ of the alkaline buffer (made by dissolving 0.21g NaHCO₃ and 0.27g Na₂CO₃ in 100 cm³ of distilled water) and make up to the mark with distilled water. Mix thoroughly.

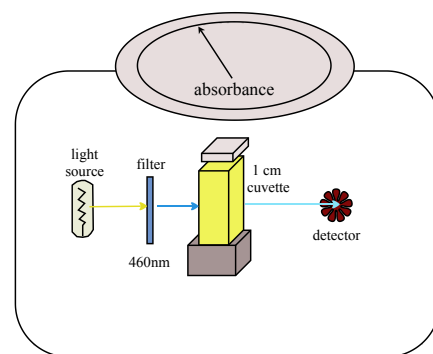
By diluting the alkaline 0.10M potassium chromate make up the following:

0.050, 0.025, 0.0125, 0.00625, and 0.0031 M solutions.

Measure the absorbance of each of these solutions in a colorimeter.

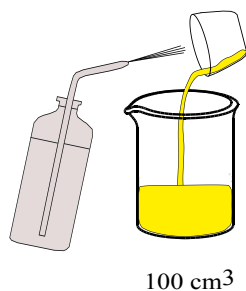
Try a blue filter (450 nm).

Obtain a calibration curve of *absorbance* versus *concentration* (mol dm⁻³).



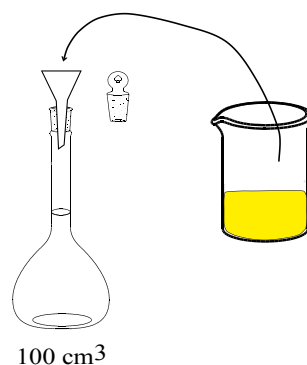
continued:

2.



Using distilled water, wash the entire contents of the crucible into a beaker.

3.



Wash the contents of the beaker into a graduated volumetric flask. Add 10 cm³ of the alkaline buffer, used previously in stage 1, and make up to the mark with distilled water. Mix thoroughly.

4.

Measure the absorbance of the solution prepared in stage 3. Use the calibration curve obtained previously to estimate the chromate concentration of this solution. Calculate the mass of potassium chromate in the total 100 cm³ of chromate solution. This is the mass of potassium chromate in the crucible after decomposition of the complex. Compare this with the theoretical yield and confirm the structure of the complex.

Experiment XVIII

Preparation & Analysis of a Transition Metal Complex

Potassium Trioxalatochromium(III)

Examples of Outcomes

Preparation

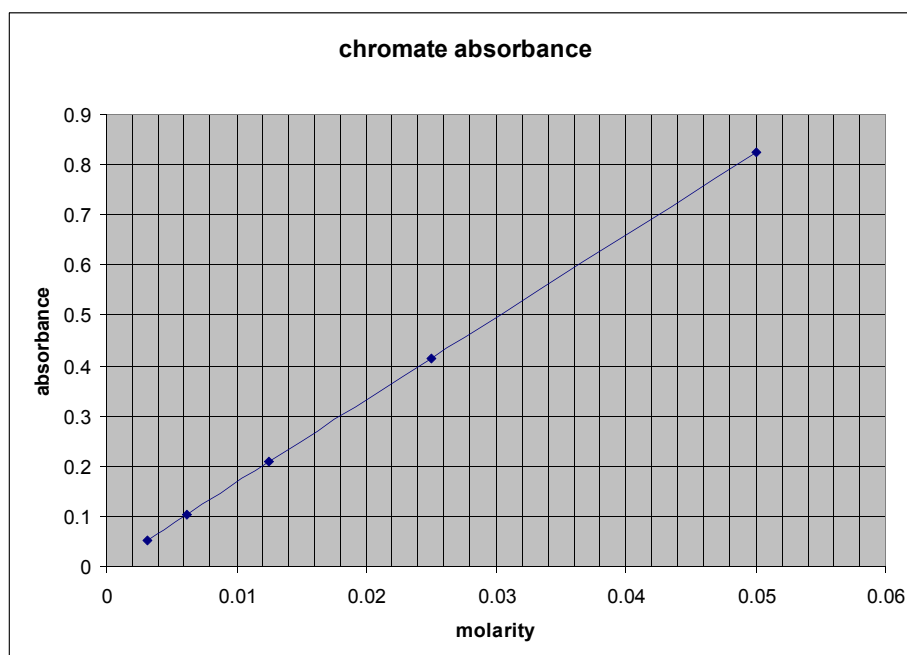
Used 1.5g of potassium dichromate. Max yield of the complex (as the trihydrate) = 4.97g.
Mass of complex obtained = 2.8g ie, $(2.8/4.97) \times 100 = 56\%$ yield.
This suggests that material was lost in the crystallisation and isolation processes.

Analysis

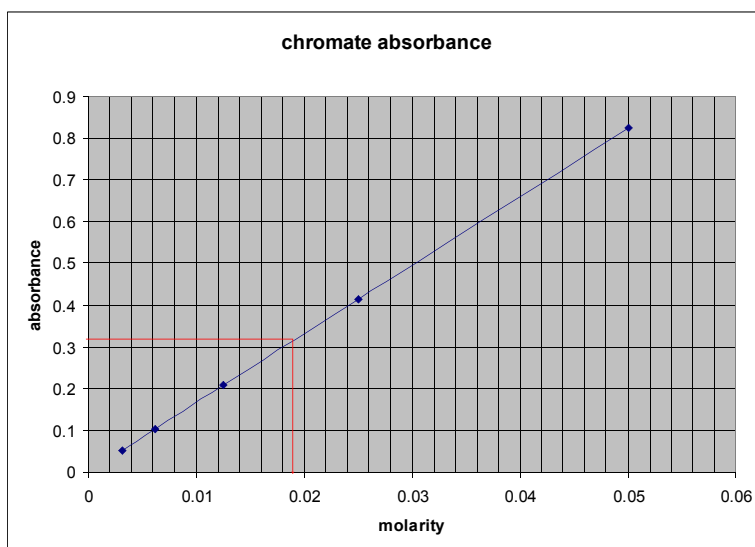
Standard chromate solutions were prepared and their absorbance values measured.
The results were plotted to provide a calibration curve.

molarity	absorbance
0.0031	0.061
0.00625	0.103
0.0125	0.207
0.025	0.413
0.05	0.825

Calibration curve



continued:



The absorbance of the chromate solution obtained from the decomposition = 0.31.

This corresponds to a molarity of 0.019, ie, 3.686g of potassium chromate per dm^3 .

Therefore mass of potassium chromate per $100 \text{ cm}^3 = 0.369\text{g}$

This compares with a theoretical mass of 0.398g.

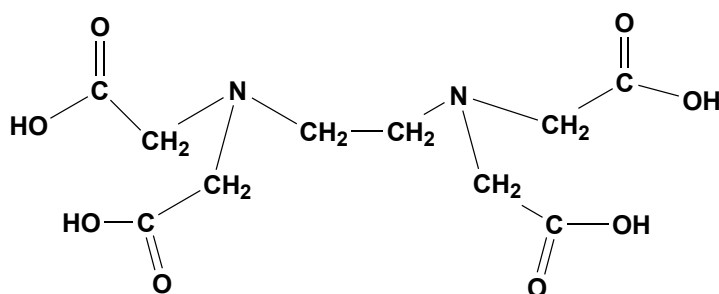
The conclusion is that, within experimental error, the prepared complex contains the amount of chromium corresponding with the given formula.

Experiment XIX

Back Titration:

Estimation of Nickel by titration against EDTA

Ethylenediaminetetraacetic acid (1,2-bis[bis(carboxymethyl)amino]ethane) in its various forms is abbreviated EDTA.



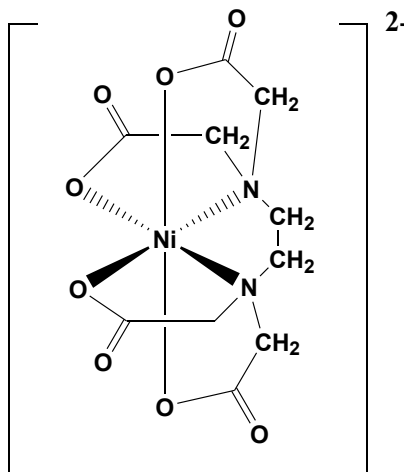
ethylenediaminetetraacetic acid
EDTA

(in the equation below, EDTA is represented by the symbol, Y))

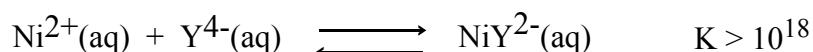
Under suitable, conditions EDTA forms 1:1 complexes with a large number of metal ions.

eg,

The 4 carboxylate groups and the 2 nitrogen groups donate pairs of electrons to the central nickel ion.



In this Ni-EDTA complex the EDTA anion (Y^{4-}) is rapped around the Ni^{2+} ion to form an octahedral complex. In aqueous solution, at pH values above 4, this complex is very stable.

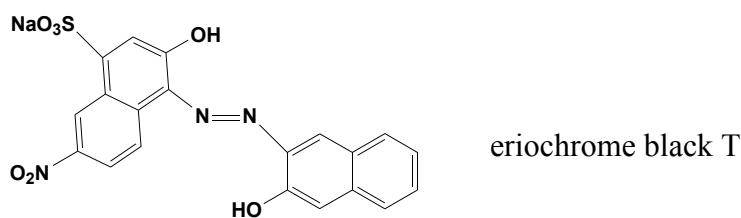


Since it is known that one mole of EDTA reacts quantitatively with 1 mole of metal ion, titrimetric analysis can be used to estimate the amount of metal ion in aqueous solution. Since the disodium salt of EDTA ($Na_2H_2Y \cdot 2H_2O$) is much more soluble in water than the parent tetraacid, it is used make up the titrant.

To detect the end point, in these titrations, metal ion indicators are used.

continued:

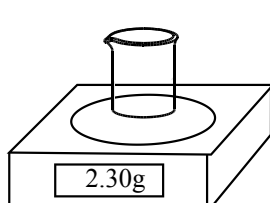
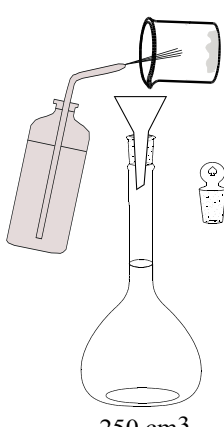
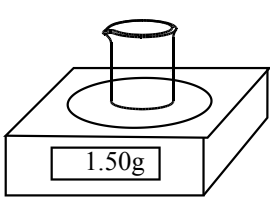
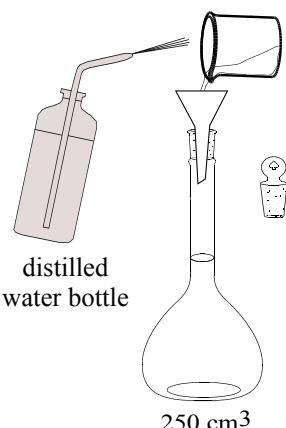
A variety of metal ion indicators are available. When making a choice it is important to select one which gives good colour contrasts and forms metal-indicator bonds which can be broken by EDTA. Eriochrome Black T (also called Solochrome Black T), for example, is *not* a good indicator for the *direct* titration of nickel because EDTA is unable to displace the metal from the metal-indicator complex. This means that the indicator is *blocked* by the metal and the required colour change at the end point (ie, red to blue) is not observed.



An interesting way round this problem is to estimate the nickel by *back titration*. A known quantity of the nickel solution is mixed with a known, **excess**, of standard EDTA solution. Buffer solution (about pH 10) is added and a few drops of eriochrome black T indicator solution. The excess EDTA is then titrated with standard magnesium sulphate solution (red end point).

Procedure:

Stage I: Preparation & Standardisation of EDTA solution.

1.  Weigh out 2.3g of the disodium salt of EDTA.
2.  250 cm³
Transfer the EDTA to the graduated volumetric flask. Add distilled water to dissolve the salt and make up to the mark with more water. Stopper and mix. This provides a solution of EDTA which is approximately 0.025M.
3.  Weigh *accurately* approximately 1.5g of AR magnesium sulphate heptahydrate. Dissolve the crystals in about 50 cm³ of distilled water taking care not to lose any material in the process.
4.  250 cm³
Carefully transfer the whole of the magnesium sulphate solution to a graduated volumetric flask. Make up to the mark with distilled water, stopper and mix. This is a solution of magnesium sulphate of accurately known concentration (ie, a standard solution of magnesium ion). Work out the molarity of your magnesium sulphate solution.

continued:

5. Prepare the indicator solution.

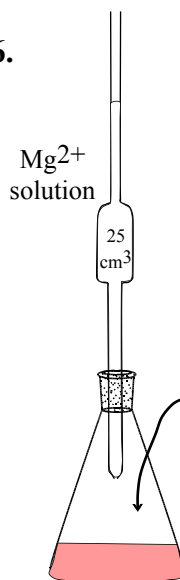
Dissolve 0.2g of eriochrome black T in 15 cm³ of triethanolamine (TEA, **irritant**) and 5 cm³ of IMS.

Store in a labelled dropping bottle.

Prepare the buffer solution (pH 10).

Add 7g of ammonium chloride to a 250 cm³ beaker. Dissolve in about 25 cm³ of distilled water. *In a fume cupboard*, add 57 cm³ of concentrated ammonia (ie, 0.88 ammonia solution). **This is corrosive and very pungent.** Make up to about 100 cm³ with distilled water. Stir and store in a sealed, labelled, container.

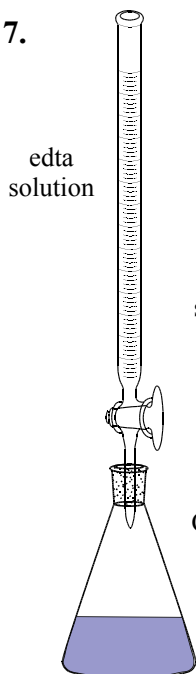
6.



Add 25.00 cm³ of standard magnesium sulphate solution to the titration flask.

Then carefully add 2 cm³ of the ammonia buffer (pH 10) and a few drops of the indicator solution (eg, 4 drops).

7.



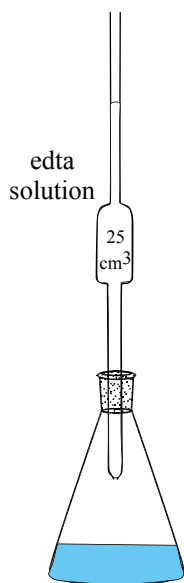
Titrate the buffered magnesium solution against the edta solution to a pure blue end point (no red tinge). Proceed slowly near the end point since complex formation is a little slow.

Repeat a number of times and calculate a mean titre. Calculate the molarity of the edta solution.

continued:

Stage II: Back titration - Estimating the concentration of a Nickel solution.

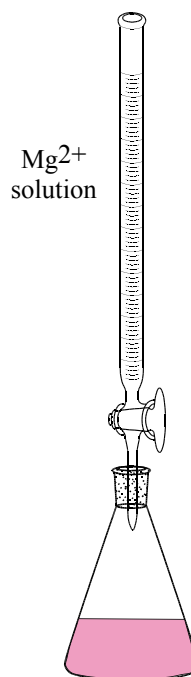
1.



Add 25.00 cm³ of standardised edta solution to the titration flask. Followed by 10.00 cm³ of the given nickel solution (which is *approximately* 0.025M).

Then carefully add 2 cm³ of the ammonia buffer (pH 10) and a few drops of the eriochrome indicator solution (eg, 3 drops).

2.



Titrate the buffered excess edta solution against the standard Mg²⁺ solution to a pure wine red end point. Proceed slowly near the end point since complex formation is a little slow.

Repeat a number of times and calculate a mean titre.

Calculate the molarity of the excess edta solution.

Calculate the amount of edta reacted with the nickel and hence the amount of nickel in 10 cm³ of nickel solution. State the molarity of the nickel solution.

continued:

Experiment XIX

Back Titration:

Estimation of Nickel by titration against EDTA

Examples of Outcomes

Stage I: Molarity of the edta solution

Mass of *disodium* edta = approx. 2.31g (ie, $(2.31/372.25) = 0.006206$ mol)

Mass of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O} = 1.52\text{g}$ (ie, $(1.52/246.3) = 0.006166$ mol)

Molarity of magnesium sulphate solution = $0.006166 \times 4 = 0.02467$ M.

Mean edta titre = 24.80 cm^3

Molarity of the edta solution = $(25.00/24.80) \times 0.02467 = 0.0249$ M

Stage II: Estimating the concentration of a nickel solution by back titration.

25.00 cm^3 of 0.0249M edta used, ie, $(25/1000) \times 0.0249 = 6.23 \times 10^{-4}$ mol.

Mean magnesium sulphate titre = 15.10 cm^3

Moles of Mg^{2+} used = $(15.10/1000) \times 0.0247 = 3.73 \times 10^{-4}$ mol

Moles of edta reacted with the $\text{Mg}^{2+} = 3.73 \times 10^{-4}$

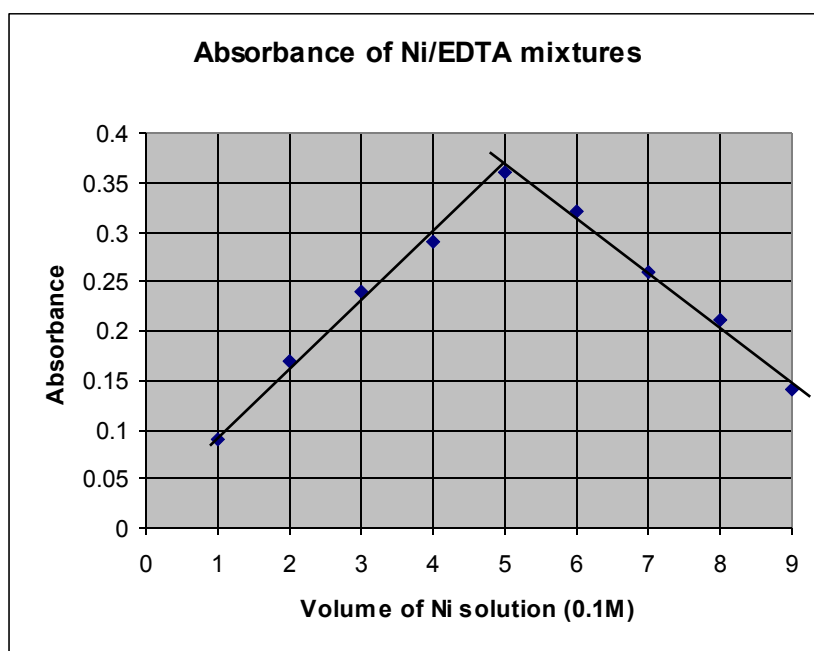
Moles of edta reacted with the $\text{Ni}^{2+} = 6.23 \times 10^{-4} - 3.73 \times 10^{-4} = 2.5 \times 10^{-4}$ mol

Moles of Ni^{2+} in 1000 cm^3 of the nickel solution = $(1000/10) \times 2.5 \times 10^{-4} = 0.025\text{mol}$ (ie, 0.025M)

An additional exercise to establish the stoichiometry of the Ni(II) - Edta reaction

A series of nickel-edta mixtures are made up and their absorbance values measured. The results are plotted to reveal the molar ratio giving the most intense colour. This indicates the combining molar ratio in the Ni-EDTA complex.

Volume of 0.1M EDTA (cm ³)	Volume of 0.1M aqNi ²⁺ (cm ³)	Absorbance
9	1	0.09
8	2	0.17
7	3	0.24
6	4	0.29
5	5	0.36
4	6	0.32
3	7	0.26
2	8	0.21
1	9	0.14



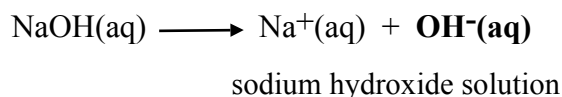
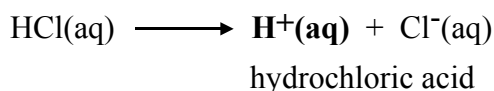
Result indicates that Ni²⁺ and EDTA combine in a 1:1 molar ratio

Experiment XX

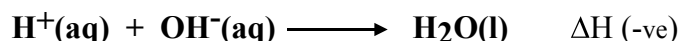
To find the Molarities of Strong and Weak acids and their Enthalpies of Neutralisation by Thermometric Titrations

Strong acids and bases are completely dissociated into their ions in dilute aqueous solution.

eg,

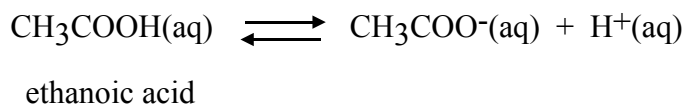


When a strong acid, such hydrochloric acid, is added to a strong base, such as sodium hydroxide, an **exothermic** reaction occurs between hydrogen ion and hydroxide ion to give water.



The salt of the acid/base reaction, sodium chloride, is also completely dissociated in solution so the sodium ions and chloride ions remain unchanged (ie, *spectator ions*). The enthalpy change is independent of these spectator ions and entirely due to the formation of water.

Weak acids, like ethanoic acid, are only partially dissociated in aqueous solution.



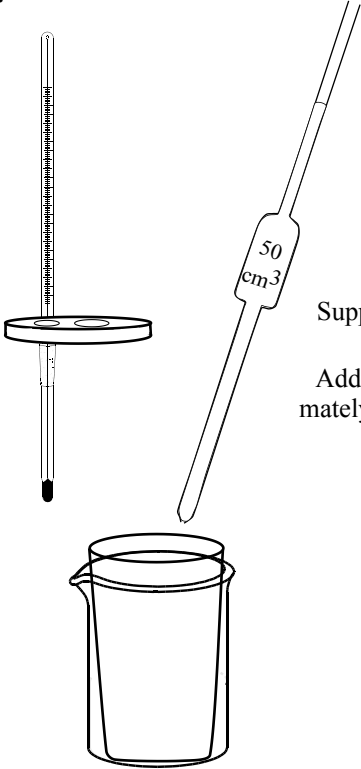
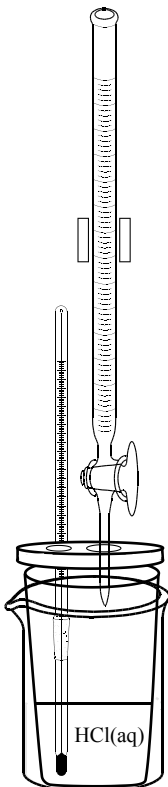
The equilibrium lies to the left in favour of undissociated acid. When this acid is reacted with sodium hydroxide solution, once again, water is the product but the reaction is **less** exothermic because energy is required to dissociate the acid *before* liberated hydrogen ion can react with hydroxide ion.

In this experiment titrate approximately 1M hydrochloric acid against standard 2.0M sodium hydroxide. Note the temperature of the reaction mixture at each addition of sodium hydroxide solution. Plot the results (temperature against volume of sodium hydroxide added) and find the maximum temperature rise (ΔT). Determine the end point and calculate the molarity of the hydrochloric acid. Calculate the enthalpy of neutralisation of hydrochloric acid.

Repeat the exercise using approximately 1M ethanoic acid. Comment on the results.

continued:

Wear protective spectacles.

- 1.
- 
- Support a plastic cup in a beaker.
Add 50.00 cm³ of approximately 1M hydrochloric acid to the cup.
- 250 cm³ beaker
- 2.
- 
- Place over the cup a loose fitting plastic lid.
Insert a 0-50°C thermometer and position a 50 cm³ burette containing the 2.0M sodium hydroxide (**CARE: this reagent is corrosive to the skin**) over the cup.
- Record the temperature of the acid to the nearest 0.1°C.
Add successive 5 cm³ aliquots of the alkali from the burette. After each addition stir the mixture with the thermometer and record the temperature (do not remove the thermometer). Add up to 50 cm³ of the alkali.
Tabulate your results.

- 3.
- Plot a graph of temperature against volume of alkali added.
Determine the end point.
Calculate the molarity of the acid.
Calculate the enthalpy of neutralisation given the following,

Enthalpy change = $\Delta T \times \text{total volume at neutralisation point} \times \text{heat capacity of the solution}$

$$\text{Heat capacity of the solution} = 4.2 \text{ J } ^\circ\text{C}^{-1} \text{ cm}^{-3}$$

4. Repeat the exercise using approximately 1M ethanoic acid instead of hydrochloric acid.

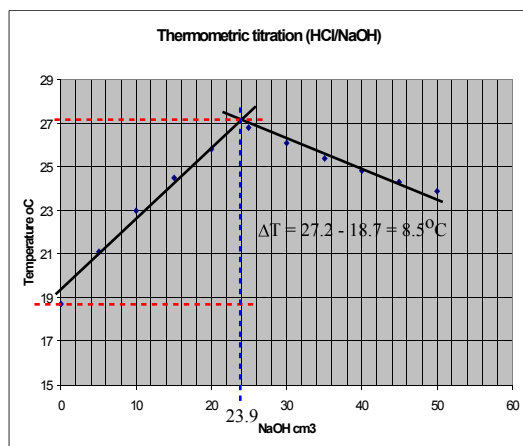
Experiment XX

To find the

Molarities of Strong and Weak acids and their Enthalpies of Neutralisation by Thermometric Titrations

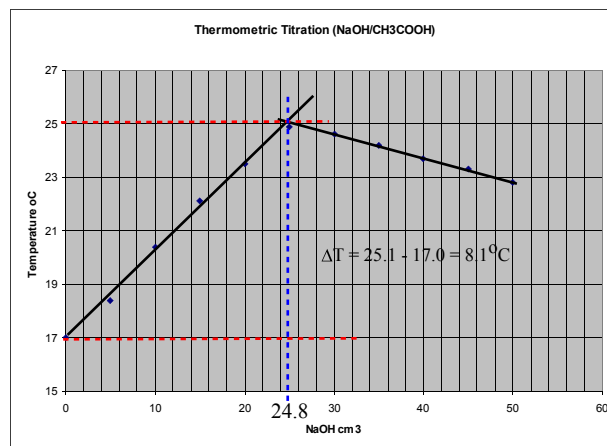
Examples of Outcomes

Hydrochloric acid	
Volume of 2M NaOH cm ³	°C
0	18.7
5	21.1
10	23.0
15	24.5
20	25.8
25	26.8
30	26.1
35	25.4
40	24.8
45	24.3
50	23.9



End point = 23.9 cm³ 2M NaOH
Molarity of HCl(aq) = $(23.9/50) \times 2 = 0.97\text{M}$
Enthalpy change = $8.5 \times 73.9 \times 4.2 = 2638\text{ J (exothermic)}$
Enthalpy of neutralisation = $-2638 \times 1000/(50 \times 0.97) = -54.4\text{ kJ mol}^{-1}$

Ethanoic acid	
Volume of 2M NaOH cm ³	°C
0	17.0
5	18.4
10	20.4
15	22.1
20	23.5
25	24.9
30	24.6
35	24.2
40	23.7
45	23.3
50	22.8



End point = 24.8 cm³ 2M NaOH
Molarity of HCl(aq) = $(24.8/50) \times 2 = 0.992\text{M}$
Enthalpy change = $8.1 \times 74.8 \times 4.2 = 2545\text{ J (exothermic)}$
Enthalpy of neutralisation = $-2545 \times 1000/(50 \times 0.992) = -51.3\text{ kJ mol}^{-1}$

Conclusion: As expected (for the reasons previously given), the enthalpy of neutralisation for ethanoic acid is lower than for hydrochloric acid. However, both of these results are lower than the literature values. For a strong acid such as hydrochloric acid it should be near -57 kJ mol^{-1} and that for the weak acid, ethanoic acid, it should be near -55 kJ mol^{-1} . A better insulated calorimeter would help to improve the experimental enthalpy of neutralisation values.

Note: -57 kJ is the enthalpy change expected when 1 mole of water is formed from the reaction between hydrogen ion and hydroxide ion in dilute aqueous solution.